Chimica Verde | Energie Rinnovabili | Salute | Materiali | Modelling | Beni Culturali

CONFERENZA DI DIPARTIMENTO 2017

DSCTM

Department of Chemical Sciences and Materials Technology

19 - 20 OTTOBRE
ALGHERO
HOTEL CALABONA



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Atti della Conferenza del Dipartimento Scienze Chimiche e Tecnologie dei Materiali
Alghero 19-20 ottobre 2017,
a cura di **Doriano Lamba** e **Francesco Verginelli**

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19-20 Ottobre 2017, Alghero (Sassari)

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PROGRAMMA

19 ottobre 2017

10.45 - 10.50	Arrivo voli Roma e Milano	
11.30	Trasferimento dall'Aeroporto di Alghero al Hotel Calabona	
12.15 - 13.00	Pranzo	
13.00	Registrazione	
13.20 - 13.40	INIZIO LAVORI	Maurizio Peruzzini
13.40 - 13.50	Chimica Verde - Introduzione	Mauro Marchetti - ICB
13.50 - 14.05	"Progettazione, Proprietà e Applicazione di Molecole σ-hole-attive in Soluzione: un Nuovo Strumento per la Chimica Sostenibile"	Peluso Paola - ICB
14.05 - 14.20	"Continuous Flow Synthesis of Fine Chemicals Over Unconventional Monolithic Catalysts"	Barbaro Pierluigi - ICCOM
14.20 - 14.35	"Valorizzazione Catalitica di Scarti dell'Agro-Industria"	Zaccheria Federica - ISTM
14.35 - 14.50	"Fine-tuning of Biocatalytic Particles by Membrane Emulsification Technology"	Piacentini Emma - ITM
14.50 - 15.20	Coffee break	
15.20 - 15.35	10 anni di attivitá del European Research Council: obiettivi raggiunti ed opportunitá per il CNR.	Favaro Monica - ERCEA-ICMATE
15.35 - 15.45	Energia Rinnovabile - Introduzione	Sanson ISTEC - Mordini ICCOM
15.45 - 16.00	"Towards a Hydrogen Economy: Low-temperature Aqueous-phase Methanol Dehydrogenation to Hydrogen and Carbon Dioxide – Mechanistic Insights"	Alberico Elisabetta - ICB
16.00 - 16.15	"Polyaniline-Carbon Nanohorn Composites as Thermoelectric Materials"	Famengo Alessia - ICMATE
16.15 - 16.30	"Mechanochemical Activation of Natural Kaolins: a Sustainable, Low Carbon, Process for the Synthesis of Geopolymeric Cements"	Ciccioli Piero - IMC
16.30 - 16.45	"Engineered PVDF-$BaTiO_3$ Composites as Efficient Dielectric Materials for Energy Storage"	Stagnaro Paola - ISMAC

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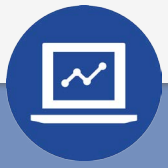
16.45 - 16.55	Salute e le Scienze della Vita - Introduzione	Palmieri ICB - Lamba IC
16.55 - 17.10	"Progettazione e Sviluppo di Biopolimeri di PNA Mimici del miR-34a nel Trattamento del Neuroblastoma"	Moccia Maria - IC
17.10 - 17.25	"Click Strategies for Oriented, Multivalent and Conformationally Controlled Immobilization of Peptide Bioprobes on Analytical Surfaces"	Gori Alessandro - ICRM
17.25 - 17.40	"Magnetic Lipid Based Nanovectors for the Targeted Delivery of Sorafenib Towards Treatment of Hepatocellular Carcinoma"	Depalo Nicoletta - IPCF
17.40 - 17.55	"Biomimetic Multifunctional Nanoparticles for Nanomedical Applications"	Adamiano Alessio - ISTEC
17.55- 18.10	"Hallmarks and Research Activity of IBB-CNR (Catania Section)"	Attanasio Francesco - IBB
18.15 - 19.15	Sessione Poster	
19.30 - 20.30	Discussione Plenaria	
21.00	Cena Conviviale Hotel Calabona	

20 ottobre 2017

08.30 - 08.40	Materiali Avanzati - Introduzione	Curri IPCF - Sanson ISTEC
08.40 - 08.55	"A Tale of (supra)Molecular Architectures and Inorganic Nanostructures Towards Luminescence Based Thermometers"	Rancan Marzio - ICMATE
08.55 - 09.10	"Graphene Nanoplatelets/Poly(lactic acid) Films: Morphological Issues and Water Vapor Sorption behavior"	Russo Pietro - IPCB
09.10 - 09.25	"Nano/Microstrutture a Basso Costo per Applicazioni in Optoelettronica"	Galeotti Francesco - ISMAC
09.25 - 09.40	"Functional Organic Field-Effect Transistors: From the Realization of Bright Nanoscale Light Sources to the Implementation in the Stimulation and Sensing of Living Systems"	Toffanin Stefano - ISMN
09.40 - 09.55	"Charge Transport Behavior of Reduced Graphene Oxide: Understanding the Mechanism From Single Sheet to Thin Film"	Kovtun Alessandro - ISOF
09.55 - 10.10	"Multifunctional Smart Ceramic Materials: Ferroelectrics/ Piezoelectrics"	Galassi Carmen - ISTEC
10.10 - 10.25	Società Chimica Italiana : ruolo, attività ed opportunità	Agostiano Angela - SCI
10.25 - 11.00	Coffee break	



11.00 - 11.10	Modelling Computazionale - Introduzione	De Angelis Filippo - ISTM
11.10 - 11.25	"Il Modelling e l'Industria: Due Esperienze Positive"	Ceresoli Davide - ISTM
11.25 - 11.40	"First-principle Modeling of the Catalytic and Optical Properties of Metal (Ultra) NanoStructures"	Fortunelli Alessandro - ICCOM
11.40 - 11.55	"Melting and Sintering of Si Nanoparticles by Molecular Dynamics Simulations"	Carravetta Vincenzo - IPCF

11.55 - 12.05	Beni Culturali - Introduzione	Miliani Costanza - ISTM
12.05 - 12.20	"Smart and Sustainable Approaches for theReliable and Long-Lasting Conservation of Metal Works of Art"	Di Carlo Gabriella - ISMN
12.20 - 12.35	"Pigment-Oil interactions in Paintings: Nature and Distribution of Metal Soaps by FTIR Spectroscopy"	Rosi Francesca - ISTM
12.35 - 13.30	Sessione Poster	
13.30 - 14.30	Pausa Pranzo	
14.30 - 15.00	Presentazione Gruppo di Lavoro Progettualita' del Dipartimento	
15.00 - 15.10	Premiazione YIA2017	
15.10 - 15.30	Premio YIA2017 - Chimica Verde	
15.30 - 15.50	Premio YIA2017 - Chimica per l'Energia Rinnovabile	
15.50 - 16.10	Premio YIA2017 - Chimica per la Salute e le Scienze della Vita	
16.10 - 16.30	Premio YIA2017 - Materiali Avanzati	
16.30 - 16.45	Menzioni d'onore YIA2017 & Premiazione Posters	
16.45 - 17.00	Chiusura dei lavori	
17.30	Trasferimento in Aeroporto	
19.20 - 19.55	Partenza Voli Roma e Milano	

ABSTRACT

SOMMARIO

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CHIMICA VERDE

COMUNICAZIONE ORALE

Progettazione, Proprietà e Applicazione di Molecole σ-hole-attive in Soluzione: un Nuovo Strumento per la Chimica Sostenibile

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Negli ultimi anni, le interazioni non covalenti che ricadono nella definizione di σ-*hole bonds* (σBs) sono state oggetto di numerosi studi volti a definirne proprietà e comportamento sia allo stato solido che in soluzione. Tali interazioni hanno anche suscitato interessi multidisciplinari per lo sviluppo di applicazioni nel settore dei materiali avanzati, in organocatalisi, *molecular sensing* e *drug discovery.*[1] Tra le interazioni basate sul σ-hole, il legame ad alogeno (*halogen bond*)[2] è l'interazione non covalente che si instaura tra un atomo di alogeno, legato covalentemente e che agisce da elettrofilo, ed una specie nucleofila. Anche atomi del VI gruppo (S, Se, Te), opportunamente attivati, possono assumere la funzione di centri σ-*hole*-attivi, comportandosi da elettrofili in chalcogen bonds.[3] L'interesse intorno a interazioni basate su σ-*hole* è piuttosto recente e alcune questioni rimangono ancora aperte. In particolare, i) fattori strutturali rendono difficile l'identificazione in soluzione di σBs deboli e ii) attualmente solo poche molecole chirali aventi σ-holes come siti di riconoscimento sono state descritte. In particolare, nessun esempio di elettrofilo chirale coinvolto in *chalcogen bond* è stato finora riportato. Nell'ambito di una collaborazione bilaterale Italia/Francia, nuove molecole chirali alogenate sono state sviluppate[4-6] per lo studio in soluzione di interazioni σBs deboli, mostrando una interessante attività σ-*hole*-controllata come organocatalizzatori in reazioni di *hydrogen transfer* su legami C=N. Nell'ambito di questi studi, il primo processo di enantiodiscriminazione controllato da chalcogen bond è stato osservato mediante studio basato su tecnologia HPLC.

Parole chiave: Chiralità, HPLC, Organocatalisi, Potenziale elettrostatico, σ-hole

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1) Politzer P., Murray J. S., Clark T. Phys. Chem. Chem. Phys., 2013, 15, 11178; 2) Cavallo G., Metrangolo P., Milani R., Pilati T., Priimagi A., Resnati G., Terraneo G. Chem. Rev., 2016, 116, 2478; 3) Bauzá A., Mooibroek T. J., Frontera A. ChemPhysChem, 2015, 16, 2496; 4) Peluso P., Mamane V., Aubert E., Cossu S. J. Chromatogr. A, 2014, 1345, 182; 5) Peluso P., Mamane V., Aubert E., Dessì A., Dallocchio R., Dore A., Pale P., Cossu S. J. Chromatogr. A, 2016, 1467, 228; 6) Mamane V., Peluso P., Aubert E., Cossu S., Pale P. J. Org. Chem., 2016, 81, 8576.

Ringraziamenti: CNR, Università Ca' Foscari di Venezia (Dip. di Scienze Molecolari e Nanosistemi), *Italia*; CNRS, Université de Strasbourg e Université de Lorraine, *Francia*

Continuous Flow Synthesis of Fine Chemicals Over Unconventional Monolithic Catalysts

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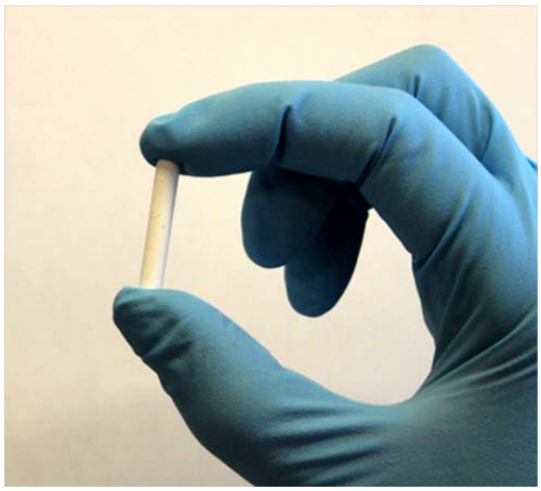
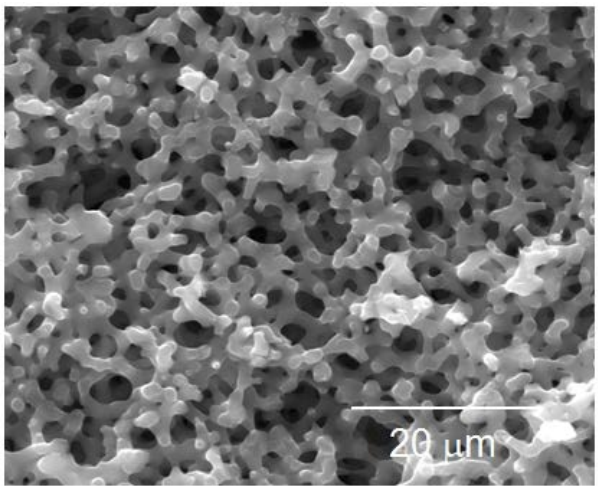
The need for a greener and sustainable process industry calls for the development of innovative materials and manufacture methods that comply with economic and environmental constraints. Herein we describe the synthesis of functionalized, meso/macro hierarchical porosity monolithic catalysts and their use the continuous flow synthesis of high added-value chemicals in the liquid phase. Various functionalities and inorganic support materials (SiO2, TiO2, Nb2O5) have been reported. The heterogeneous catalysts have show excellent performance, either in terms of activity, selectivity and durability, under very mild flow conditions, temperatures and pressures, so as to provide remarkable process intensification and flexibility compared to conventional systems. High long-term productivities have been observed both in metal-mediated hydrogenations and acid-catalyzed reactions. The production of pharmaceutical building blocks, monomers, fragrances and food additives is possible, with no need for catalysts regeneration, no products contamination by metals as well as use of water solvent.





Parole chiave: Green chemistry, heterogeneous catalysis, continuous flow, selective processes

Riferimenti:

1) F. Liguori, P. Barbaro, B. Said, A. Galarneau, V. Dal Santo, E. Passaglia, A. Feis, ChemCatChem 2017, DOI: 10.1002/cctc.201700381.
2) C. Moreno-Marrodan, F. Liguori, P. Barbaro, Beilstein J. Org. Chem. 2017, 13, 734.
3) A. Sachse, N. Linares Perez, P. Barbaro, F. Fajula, A. Galarneau, Dalton Trans. 2013, 42, 1378.
4) N. Linares, S. Hartmann, A. Galarneau, P. Barbaro, ACS Catal. 2012, 2, 2194.

Ringraziamenti: 7th FP, Marie-Curie Initial Training Network NANO-HOST (PITN-215193)
European Research Institute of Catalysis a.i.s.b.l.

Valorizzazione Catalitica di Scarti dell'Agro-Industria

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La valorizzazione di scarti e sottoprodotti derivanti dall'industria agro-alimentare rappresenta un passaggio fondamentale nella transizione verso il modello di economia circolare. In questo contesto una parte significativa della recente ricerca di ISTM, sulla base delle competenze sviluppate nell'ambito delle tecnologie per la bioraffineria, è stata rivolta all'uso della catalisi per la trasformazione selettiva di biomasse provenienti da residui della filiera agro-industriale. E' questo il caso dell'attività svolta nell'ambito del progetto RiceRes, che vede coinvolto anche l'Istituto ISMAC, volto alla valorizzazione degli scarti della produzione di riso. Dalla fase di fresatura del chicco si ottengono infatti importanti biomasse quali pula e lolla, oltre a consistenti quantitativi di paglie (1,35 Ton/ton di riso) lasciati in campo dopo la raccolta.

Nell'ambito del progetto è stata studiata la possibilità di usare le paglie per migliorare le proprietà meccaniche di materiali isolanti a base di lana di scarto, così come l'opportunità di ricavare bio-silice dalla lolla da utilizzare come filler nella preparazione di materiali compositi a base di biopolimeri. Dalla pula è inoltre possibile estrarre discrete quantità di olio che grazie alle sue particolari caratteristiche di composizione è stato analizzato e studiato nella preparazione di bioadesivi. L'olio di pula di riso (RBO) ha inoltre la caratteristica di avere un'elevata acidità libera che ne rende difficile l'utilizzo per la preparazione di prodotti attraverso i tradizionali sistemi industriali usati in ambito oleochimico. Le competenze di ISTM sia nella lavorazione degli oli per scopi industriali, che nell'uso di catalizzatori solidi acidi ha consentito la messa a punto di alcuni processi per la preparazione di prodotti di interesse per diversi settori dell'industria chimica a partire da RBO sfruttando principalmente reazioni di esterificazione. Tra questi la preparazione di monogliceridi, largamente utilizzati come emulsificanti e surfactanti [1], sterolesteri, impiegati come cibi funzionali, e resine.
Dopo separazione dell'olio dalla pula è possibile inoltre estrarre e valorizzare la frazione proteica producendo idrolizzati per l'industria alimentare o cosmetica.
Il modello di bioraffineria degli scarti applicato alla manifattura del riso è per di più applicabile a diverse altre filiere di notevole impatto quale per esempio quella lattiero casearia, nell'ambito della quale l'uso della catalisi eterogenea ha consentito la preparazione di zuccheri ridotti attraverso un processo di idrolisi + idrogenazione a partire da lattosio, importante componente del siero di latte [2].

Parole chiave:
Scarti agro industriali, bioraffineria, catalisi eterogenea, oleochimica

Riferimenti:
[1] M. Mariani, F. Zaccheria, N. Scotti, R. Psaro, N. Ravasio, ChemistrySelect 2016,1(12), 2999;
F. Zaccheria, M. Mariani,N. Ravasio, Chem.Biol.Technol.Agric. 2015 , 2:23;
[2] F. Zaccheria, M. Mariani, N. Scotti, R. Psaro, N. Ravasio, Green Chem., 2017, 19,1904

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Fine-tuning of Biocatalytic Particles by Membrane Emulsification Technology

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Enzyme applications have a considerable role at the heart of biotechnological processes. Improvements in enzyme formulation are required to significantly broaden the application of biocatalyst for the environmentally friendly synthesis of fine chemical products. A large number of these biotechnological processes require successful enzyme immobilization in terms of resistance to leaking, retention of enzyme activity over long-term storage, operational stability under adverse environmental conditions, accessibility to substrates, fast catalysis, and, in general, proper enzyme immobilization density with adequate orientation. Membrane emulsification (ME) is emerging as a more promising formulation method to produce monodisperse particles in mild operative conditions and with low energy consumption [1].
In the present work, ME was used for simultaneously prepare polyvinyl alcohol (PVA) microspheres and phase transfer biocatalyst immobilization [2]. Lipase has been used as a model interfacial biocatalyst to demonstrate the powerful of the use of membrane emulsification mechanism in the production of carriers with tailored properties for enzyme immobilization. The enzyme was immobilized during particle formation (by entrapment) achieving an oriented immobilization of the enzyme. During the formation of the W/O emulsion, the lipase distributed at the W/O interface, and exhibited its open (active) form in which the catalytic site is accessible to the substrate. The addition of a crosslinking agent during the solidification step “freezed” the enzyme in its active form. The entrapment method permitted obtaining a specific activity comparable with the one of the free enzyme and the enzyme activity remained approximately constant over time in repeated cycles of reaction. The entrapment method by ME has been compared with other immobilization methods (i.e adsorption, cross-linking). Data demonstrated that the entrapment did not affect enzyme intrinsic biocatalytic activity, whilst allowing at the same time confinement with balance between molecular mobility and heterogenization. The basic mechanism and best operating conditions for fine-tuning biocatalytic particles construction (particle size, particle size distribution and structure) will be described.
Results demonstrated that ME can be used to implement the development of bio-functionalized micro-nanostractured devices with improved functions, sensitivity, and stability for sustainable bioproduction of pharmaceutical, food and cosmetic products.

Parole chiave: membrane emulsification, enzyme immobilization, entrapment, white biotechnology, biocatalytic particles, lipase, sustainable bioproduction.

Riferimenti:

1) Piacentini, E., Drioli, E., Giorno, L., J. Membr. Sci., 468, 410-422 (2014).
2) Piacentini, E., Yan, M., Giorno, L. J. Membr. Sci., 524, 79-86 (2017).

Ringraziamenti: The authors acknowledge for the financial support the project PON01_01545, Olio più, within the framework PON Ricerca e Competitività 2007–2013.

ENERGIA RINNOVABILE

COMUNICAZIONE ORALE

Towards a Hydrogen Economy: Low-temperature Aqueous-phase Methanol Dehydrogenation to Hydrogen and Carbon Dioxide – Mechanistic Insights

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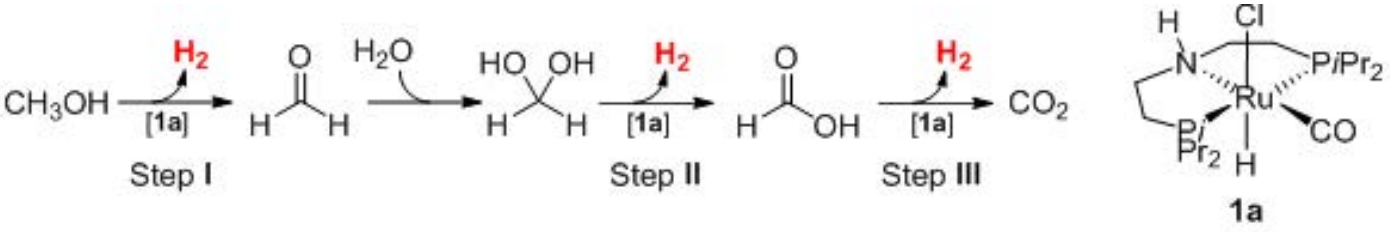
Hydrogen produced from renewable resources is a promising potential source of clean energy. Its physical properties though render its handling and transportation problematic. Its chemical storage in an organic liquid might be a viable option to overcome these difficulties. Methanol is considered to be the most promising among the organic liquid hydrogen carriers, as it is liquid at room temperature and has a comparatively high H_2 content (12.6 wt %), which can be released through steam reforming.
Recently we have shown that ruthenium[1] and iron[2] PNP-pincer complexes are competent catalysts for the dehydrogenation of methanol under relatively mild conditions, as they can catalyze all the three steps through which this transformation occurs. In particular, the ruthenium PNP complex **1a** {RuH(CO)Cl[HN(C_2H_4Pi-Pr_2)$_2$]} represents a state-of-the-art catalyst for the low-temperature (<100 °C) basic aqueous methanol dehydrogenation to H_2 and CO_2, achieving excellent catalyst turnover frequencies (4,700 per hour) and turnover numbers (exceeding 350,000).[1]



Here we would like to report on our latest investigations that, through combination of experiment, spectroscopy and theory, have provided insights into the mechanism of **1a** promoted methanol dehydrogenation and a rational for the need of high base concentration to achieve high activity.[3]

Parole chiave: Hydrogen, Methanol, Ruthenium, Iron

Riferimenti:

1) M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller *Nature* **2013,** 495, 85 – 89; 2) E. Alberico, P. Sponholz, C. Cordes, M. Nielsen, H.-J. Drexler, W. Baumann, H. Junge, M. Beller, *Angew. Chem., Int. Ed.* **2013,**52, 14162−14166; c) E. Alberico, A. J. J. Lennox, Lydia K. Vogt, H. Jiao, W. Baumann, H.-J. Drexler, M. Nielsen, A. Spannenberg, M. P. Checinski, H. Junge, M. Beller J. *Am. Chem. Soc.* **2016**, 138, 14890−14904

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This work has been carried out in collaboration with Prof. Matthias Beller and his group at the Leibniz Institut für Catalyse, Rostock, Germany: Dr. Henrik Junge, Dr. Alastair Lennox, Dr. Lydia Vogt, Dr. Martin Nielsen, Dr. Haijun Jiao.

Polyaniline-Carbon Nanohorn Composites as Thermoelectric Materials

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Thermoelectric (TE) materials can convert heat into electricity when a temperature gradient is present. The investigation of conductive polymers such as polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT) as active materials for thermoelectric generators in the room temperature range is gaining interest because of several key advantages offered by these materials. The relative easiness of solution processing, their mechanical stability and flexibility together with low density and low thermal conductivity make conductive polymers suitable for integration in a thermoelectric generator. Polymers offer remarkably low thermal conductivity values but modest Seebeck coefficient and electrical conductivity. In this work, polymer/inorganic nanocomposites of PANI with carbon particles such as single wall carbon nanohorns (SWCNHs) were prepared via solution mixing of the precursors in order to increase the electrical conductivity by means of polymer matrix/NH electronic junction. Electrical conductivity, Seebeck coefficient and through plane thermal conductivity were estimated on PANI/SWCNHs composites. Thermal stability of PANI/SWCNHs composites was evaluated by means of thermogravimetric analysis/differential scanning calorimetry coupled with residual gas analysis.

Parole chiave: thermoellectric materials, conductive polymers, polyaniline, carbon nanohorn

Mechanochemical Activation of Natural Kaolins: a Sustainable, Low Carbon, Process for the Synthesis of Geopolymeric Cements

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According to the roadmap defined for the year 2020 by the European Union (EU) Commission for a resource efficient Europe [1], the reduction of greenhouse gases from industrial processes is a priority task. In the EU countries, most of these emissions come from the ETS sector, where cement industry is one of the most important. The case of Italy is paradigmatic. With 0,35 Mt y^{-1} of CO_2 [2], Italy is one of the major CO_2 emitting countries in Europe, and is ranked as 19th in the world. The major role played by the cement industry in Italy comes by the fact that Italy is the second cement producer in Europe [3]. High emission of CO_2 occurs in cement production, because the primary component of cement (clinker) is obtained by heating at 1450°C stoichiometric mixtures of carbonate and silico-aluminate rocks in rotary kilns. For this reason, an increasing number of research programmes in the field of advanced materials is recently devoted to test the suitability of non-hazardous decarbonized materials (e.g. fly ash, volcanic tuffs) as partial substitutive of clinker in cement formulations as well as to develop new, low-carbon, cementitious binders.

Among these novel cements, Si-Al geopolymers [4] are the most promising for the years to come, as they could completely replace clinker. While clinker uses the hydraulic reaction to form a nanomaterial with randomly oriented hydrated calcium silicates, several Si-Al materials can rapidly react in alkaline solutions. This approach is more flexible than that the hydraulic one, because different 2D and 3D polymers can be obtained as a function of the Si/Al ratio of the reagent and the type of compensatory cations introduced in the structure. The general formula of geopolymers can be written as:

$$C.[-(SiO_2)z\text{-}AlO_2\text{-}]n\ .wH_2O$$

Where C is a monovalent or divalent cation, z is an integer from 1 to 3, n is the degree of polycondensation, and w the water molecules coordinated by the structure. Depending on the Si/Al ratios and C, nano-materials made of randomly oriented Si-Al crystals displaying different thermal and mechanical properties can be formed.

Metakaolins (MKAs) are the most used materials in the synthesis of Si-Al based geopolymers [4]. MKAs are amorphous materials obtained by dehydration of natural kaolins, where kaolinite crystals are, by far, the dominant mineral. Dehydration of kaolinite is usually performed by heating kaolins at temperatures ranging from 650 to 800°C for more than 2 hours. The CO_2 emission produced by burning fuel to heat the kilns for the thermal treatment of kaolins makes the Si-Al based geopolymer production less environmentally sustainable.

Although it is known that kaolins can also be converted into MKAs by grinding them in mills whose moving masses rotate at high speeds (800 to 2.000 r.p.m.) [5], the potential of mechanochemical processing of kaolins for the synthesis of Si-Al geopolymers still needs to be better investigated. With the MECAGEOPOLY CNR-MIUR Flagship Project, coordinated by IMC, we wanted to demonstrate the feasibility of mechano-chemical processing in producing Si-Al geopolymeric binders at an industrial level, in order to further reduce CO_2 emission. The mechanochemical treatment was investigated using a kaolin whose thermal behavior was

known. The material was grinded under different conditions and times, and the various MKAs obtained were characterized by XRD, FTIR-AR, TGA-DTG-DTA, ^{27}Al, ^{29}Si and 1H MAS NMR, and other techniques. The ability of mechanically activated MKAs to make Si-Al geopolymers was thus investigated, and the chemical, mechanical and thermal properties of the obtained products determined. The results of this study will be presented and critically discussed.

Parole chiave: Mechanochemistry, Low carbon cements, Geopolymers, Supplementary cementitious materials.

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Engineered PVDF-$BaTiO_3$ Composites as Efficient Dielectric Materials for Energy Storage

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The request for high energy density capacitors has largely grown in recent years in parallel with the rapid development of the electronic industry and the need of storing electrostatic energy more efficiently. To this purpose, high dielectric constant materials can be achieved by combining into a composite different materials with proper characteristics.[1] Indeed, ferroelectric particles, such as barium titanate ($BaTiO_3$), with high dielectric constant (k ≈ 1000) embedded into a polymer matrix (k 3÷10) significantly increase the relative dielectric constant of the resulting composite, while maintaining desirable properties of the polymer, such as processability, flexibility, and high dielectric breakdown field.[2] The ultimate properties of these dielectric materials, however, are strongly influenced by dimensions and morphology of inclusions as well as by their dispersion and adhesion to the polymer matrix. Surface engineering of ceramic particles can therefore play a key role in minimizing particle-particle interaction enhancing particle-polymer interaction and reducing dielectric losses.

Here, $BaTiO_3$ nanoparticles (100÷150 nm), prepared in-house by a hydrothermal-like method starting from $BaCl_2$ and $TiCl_4$ precursors,[3] were dispersed into a matrix of poly(vinylidene fluoride) (PVDF, Solef 6008 Solvay). 0-3 connectivity composites containing up to 35 vol% of ceramic inclusions were obtained either by solution casting or melt blending in a Brabender type batch-mixer; a compression moulding step was performed to obtain sheets 0.5-1 mm thick enriched in the electro-active β polymorph of PVDF. Bare and surface-modified $BaTiO_3$ particles were used, modification included functionalization with silane-based coupling molecules and/or coating with a thin shell of TiO_2 (k ≈ 100). Such engineered polymer/ceramic interfaces should facilitate a fine dispersion of the inclusions by realizing, from the particle core to its surface, a gradient of the dielectric constant giving a more homogeneous distribution of the electric field in the resulting composites.

Morphological and microstructural features of particles and composites were investigated by TEM and SEM-EDX microscopy, respectively. The amount of the ferroelectric crystalline β phase in the PVDF matrix was determined by ATR-FTIR spectroscopy and X-ray diffraction. The dielectric constant and the loss tangent of the composites were measured at different frequencies by impedance spectroscopy. Simulations of electric field distribution performed by 3D finite element modelling were correlated with the experimental evidences.

Keywords: $BaTiO_3$ nanoparticles; PVDF composites; surface modification; dielectric properties.

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SALUTE

COMUNICAZIONE ORALE

Progettazione e Sviluppo di Biopolimeri di PNA Mimici del miR-34a nel Trattamento del Neuroblastoma

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Il neuroblastoma è il più comune tumore solido extra-cranico ed è responsabile del 15% di mortalità infantile. La sovraespressione del proto-oncogene MYCN rappresenta il *biomarker* più significativo della malattia e risulta amplificato nel 25% dei tumori di neuroblastoma.[1] La sovraespressione di MYCN ha effetti catastrofici sulla biologia della cellula tumorale, la cui crescita diviene incontrollata. Recentemente è stato dimostrato che il miR-34a lega il 3'UTR dell' mRNA di MYCN bloccando l'espressione della proteina.[2] La struttura del miR-34a è stata pertanto scelta come modello (*lead compound*) per il *design* di sequenze analoghe in PNA per inibire la traduzione in proteina dell'*m*-RNA di MYCN. In virtù delle proprietà specifiche, quali alta affinità e specificità nel legare l' RNA e la stabilità metabolica,[3] i PNA sono stati identificati come analoghi sintetici in grado di "mimare" l'azione di miR-34a. La risposta alla domanda sulla dimensione minima richiesta per l'efficacia e' un dato cruciale ai fini della comprensione del meccanismo di *silencing* e un' informazione essenziale per lo sviluppo di nuove molecole. Sono state preparate sequenze di PNA-34a di diversa lunghezza; è stata dimostrata la loro capacità di legare i 2 siti di legame dell'mRNA di MYCN sia attraverso studi di UV e CD (determinazione della stabilità e conformazione dei complessi) sia *in silico* attraverso il pacchetto di simulazione Gromacs di dinamica molecolare. Studi preliminari in vitro sono stati condotti sul cellule di neuroblastoma Kelly, che contengono un'amplificazione di MYCN; in particolare si sono eseguiti studi di internalizzazione, di vitalità cellulare e di microscopia confocale.

Parole chiave: Neuroblastoma; MYCN, miRNA-34a, PNA.

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Ringraziamenti:

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Click Strategies for Oriented, Multivalent and Conformationally Controlled Immobilization of Peptide Bioprobes on Analytical Surfaces

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The generation of robust analytical data using microarray platforms strictly relies on optimal ligand-target interaction at the sensor surface which, in turn, is inherently bound to the correct immobilization scheme of the interrogated bioprobes. In the presented work, we performed a rigorous comparative analysis of the impact of peptide ligands immobilization strategy in diagnostic serological tests. We generated arrays of peptide probes that were selectively oriented on polymeric coatings by means of different click-type reactions, and we compared immobilization efficiency and diagnostic performances among the different chemoselective reactions. Moreover, we investigated the effect of multiple epitope presentation (MEP) and we analysed the role of fine tuning of the surface peptide density in the generation of a reliable and consistent analytical outcome. Finally, we evaluated the role of peptide structural stabilization in order to gain improved diagnostic efficiency. Overall, our findings clearly support the favorable role of correct bioprobes orientation in generating more reliable and reproducible data. We then demonstrated that a fine tuning of the surface peptide density plays a crucial role to fully exploit the potential of oriented and multiple peptide display, and we assessed that a multiple presentation allows for a more efficient characterization of antibodies-binding fingerprints at a statistically significant level. At last, we demonstrated that peptide epitope structural stabilization is a viable way to obtain more efficient diagnostic tools.

Parole chiave: Peptides, Microarray, Click chemistry, Diagnostics, Microanalytics

Riferimenti:

A. Gori*, M. Cretich*, R. Vanna, L. Sola, P. Gagni, G. Bruni, M. Liprino, F. Gramatica, S. Burastero, M. Chiari - **Analytica Chimica Acta,** 2017, 983: 189-197; *"Multiple epitope presentation and surface density control enabled by chemoselective immobilization lead to enhanced performance in IgE-binding fingerprinting on peptide microarrays "*

A. Gori, L. Sola, P. Gagni, G. Bruni, M. Liprino, C. Peri, G. Colombo, M. Cretich*, M. Chiari - **Bioconj Chem**, 2016, 27(11), 2669-2677; *"Screening complex biological samples with peptide microarrays: the favorable impact of probe orientation via chemoselective immobilization strategies on clickable polymers "*

A. Gori*, C. Peri, G. Quilici, A. Nithichanon, D. Gaudesi, R. Longhi, L. Gourlay, M. Bolognesi, G. Lertmemongkolchai, G. Musco, G. Colombo* - **ACS Infect Dis**, 2016, 2(3), 221-230; *"Flexible vs rigid epitope conformations for diagnostic- and vaccine- oriented applications: novel insights from the Burkholderia pseudomallei BPSL2765 Pal3 epitope "*

A. Gori*, R. Longhi - **Methods in Molecular Biology**, 2016, 1352: 167-182; *"Chemoselective strategies to peptide and bioprobes immobilization on microarray surfaces"*

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Magnetic Lipid Based Nanovectors for the Targeted Delivery of Sorafenib Towards Treatment of Hepatocellular Carcinoma

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Hepatocellular carcinoma (HCC) is the sixth most common malignancy and is the leading cause of mortality in patients with cirrhosis. When the tumor is in an advanced stage and a radical surgery is, in most cases, no longer feasible, medical management is the only possible treatment option. Sorafenib is currently the first and sole biological agent clinically approved for patients with advanced HCC. As well as significant activity, sorafenib is characterized by severe toxic side effects and poor solubility in aqueous environment, limiting the possible therapeutic response and its application for local treatment [1]. Nanoparticle (NP) based approaches offer a valuable alternative for cancer drug delivery, thus ensuring the accumulation of high concentrations of drug to the targeted cancer cell, with a concomitant reduced toxicity of normal tissue. Superparamagnetic iron oxide NPs (SPIONs) are very attractive for delivery of therapeutic agents as they have been reported to enhance the drug delivery to specific locations in the body through the application of an external magnetic field. Here, lipid based nanoformulations containing sorafenib and SPIONs have been prepared and thoroughly investigated by means of complementary techniques, thus finally resulting effective drug delivery magnetic nanovectors with good stability in aqueous medium and high drug encapsulation efficiency [2]. In addition, the relaxometric characterization has proven that the magnetic nanocarriers loaded with sorafenib are also very efficient contrast agents, with a great potential in magnetic resonance imaging technique. The proposed magnetic nanovectors loaded with sorafenib represent promising candidates for image guided and magnetic targeting of sorafenib to liver towards an efficacious treatment of HCC.

Keywords: SPIONs, magnetic lipid based nanovectors, magnetic targeting, sorafenib

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Biomimetic Multifunctional Nanoparticles for Nanomedical Applications

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Calcium phosphates (CaPs), having chemical similarity with the mineral component of bones and teeth, are ideal materials for healthcare applications. Usually, they are used for bone repair applications due to their well-known properties of osteoinductivity, bioactivity and biodegradability. The recent progresses in the structural characterization at the nanoscale level and in the colloidal stabilization of CaPs nanocrystals have opened new perspectives in their use in nanomedicine. The chemical similarity with the mineral phase of bone can be extremely useful in nanomedicine to overcome the limitations of the currently studied nanoparticles, since CaPs can be recognized by the organism as a sort of endogenous materials. Moreover, they present other numerous interesting properties such as biodegradability, low production costs and pH-dependent dissolution. CaPs dissolve into their ionic constituents (Ca^{2+} and PO_4^{3-}), which are already present in relatively high concentration (1-5 mM) in the cells and the bloodstream. CaPs are also well-known for their capability to bind a wide variety of biomolecules due their high surface area and presence of available surface ionic sites. In this way, active targeting moieties as well as the therapeutic agents can be incorporated into the nano-devices to specifically enhance their internalization by target cells. In this presentation I will show some recent findings in this field of our research activity. In particular the preparation and characterization of CaPs even endowed with superparamagnetic features by doping with Fe(II)/Fe(III) ions as well as the possibility to functionalize them with drugs, positron emission tomographic imaging agents and active targeting moieties for the selective cells internalization, microRNAs and mimetic peptides will be displayed.

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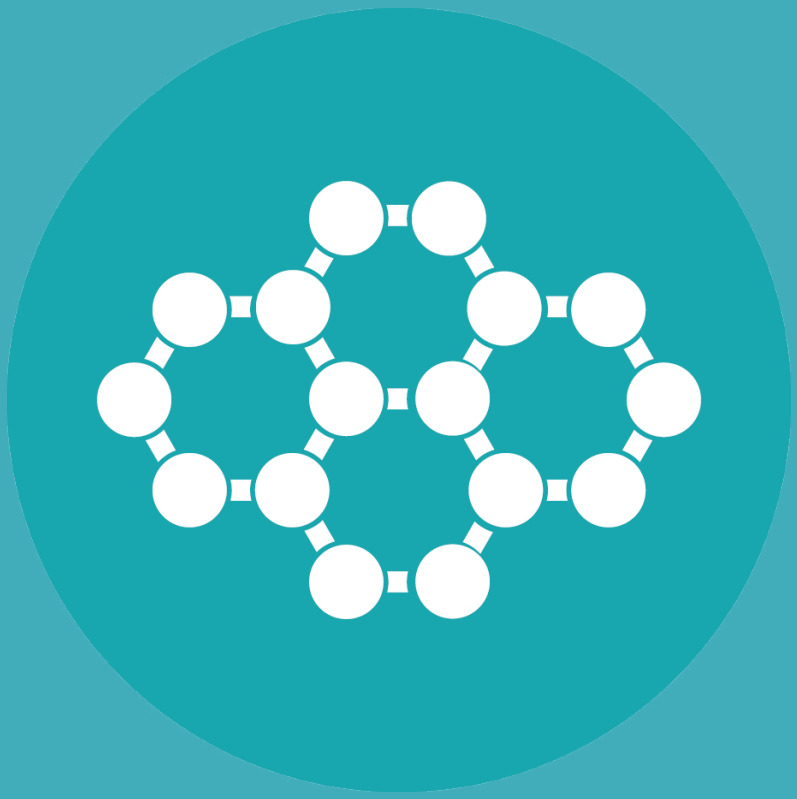
La sede secondaria di Catania dell'Istituto di Biostrutture e Bioimmagini è un centro di ricerca che coniuga le conoscenze chimiche con quelle biologiche allo scopo di investigare i meccanismi coinvolti nelle malattie umane per lo sviluppo di nuovi strumenti per la prevenzione, la diagnosi e terapie mirate. L'area chimica è costituita da ricercatori con competenze nell'ambito della chimica di sintesi, chimica analitica, chimica fisica, mentre la componente biologica vanta competenze che spaziano dalla biochimica alla biologia molecolare e cellulare.
All'interno delle due componenti, molte sono le competenze specifiche maturate grazie anche alla partecipazione a diversi progetti di ricerca. La sintesi di peptidi e la loro coniugazione con molecole di diversa natura, tecniche spettroscopiche (CD, UV-Vis, Fluorescenza), di spettrometria di massa (ESI-MS e MALDI-TOF), calorimetriche (ITC, DSC e PPC), di potenziometria e di voltammetria, e biologiche (saggi su cellule, Western Blot, citofluorimetria, microscopia confocale e widefield, modulazione dell'espressione genica tramite overespressione e RNA interferenza) rientrano tra alcune delle competenze maturate dal gruppo nel corso dell'ultimo decennio.
Un quadro di quello che sono le dotazioni in termini di infrastrutture e le principali attività di ricerca e le competenze maturate dal gruppo verrà presentato.

Parole chiave: Chimica Biologica

MATERIALI AVANZATI



COMUNICAZIONE ORALE

A Tale of (supra)Molecular Architectures and Inorganic Nanostructures Towards Luminescence Based Thermometers

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Since last few years, many efforts have been made in the development of novel non-invasive luminescence (PL) thermometers as organic, inorganic and hybrid materials that show a dependence of their PL properties on temperature. Lanthanide based systems are ideal candidates due to their peculiar emission properties.
In this context, we will show as an accurate molecular design and coordination chemistry can be used to finely tune[2] and to maximize the target functional property leading to molecular thermometers with relative thermal sensitivity values among the highest reported so far.
The molecular design beneath has proved to be crucial also to develop efficient routes to integrate such discrete molecular entities with inorganic surfaces and films[3] to build step-by-step mixed supported lanthanide species and to introduce new properties such as chirality[4] towards multifunctional hybrid materials.
In this presentation, the development of new luminescence based thermometer and their interplay with inorganic and polymeric matrices will be discussed as case study of the research activity carried out in the FMNlab at the ICMATE Institute devoted to the design, synthesis and characterization of functional systems ranging from metallo-supramolecular architectures to surfaces and inorganic nanostructures.

Key words: inorganic materials; surfaces; lanthanides; luminescence; metallo-supramolecular systems

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Graphene Nanoplatelets/Poly(lactic acid) Films: Morphological Issues and Water Vapor Sorption behavior

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Nowadays, plastics, intrinsically biodegradable or coming from renewable sources, have gained a growing popularity and an outstanding interest of the research both because of environmental and property advantages. Current applications of bio materials are in automotive, environmentally-friendly home products, fabrics, agriculture/food packaging, green building (wall coverings, draperies, furniture, paints), and more. However, their use is still restricted essentially for their relatively high cost, properties usually inferior to those characterizing petroleum based resins, difficult procurement and storage issues.
In this frame, this contribution deals with a commercial PLA grade modified by inclusion of 0.25% and 0.75% by weight of lamellar particles of graphene nanoplatelets (GNPs) reporting morphological features and water vapor sorption behavior of films produced by solvent casting.
In details, preliminarily Raman spectroscopy was employed essentially to highlight some morphological features and X-Ray diffraction measurements to highlight structural aspects. Then, the influence of GNPs on water sorption/desorption kinetics of PLA composite films was analyzed at a temperature of 35 °C and at 5 different activity levels of water from 0.1 to 0.5 using a recent approach based on in situ time resolved FTIR spectroscopy in transmission mode.
Results showed that the percolation threshold of studied samples is in the considered range of GNPs content while X-ray diffraction analyses demonstrated that studied films are essentially amorphous. Time resolved FTIR measurements, adequately substantiate by gravimetric tests, indicated a Fickian behavior for all investigated samples with diffusivity markedly affected by the level of water activity as well as a significant reduction of the water vapor up-take in presence of GNPs.

Key words: Poly(lactic acid), Graphene Nanoplatelets, Raman spectroscopy, X-Ray diffraction, FTIR

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Nano/Microstrutture a Basso Costo per Applicazioni in Optoelettronica

Francesco Galeotti, Cristina Sandionigi, Elisa Lassi, Benedetta Squeo, Francesco Carulli, Stefania Zappia, Wojciech Mroz, Erika Kozma, Marinella Catellani, Umberto Giovanella, Silvia Luzzati, Mariacecilia Pasini, William Porzio, Silvia Destri, Guido Scavia, Chiara Botta.

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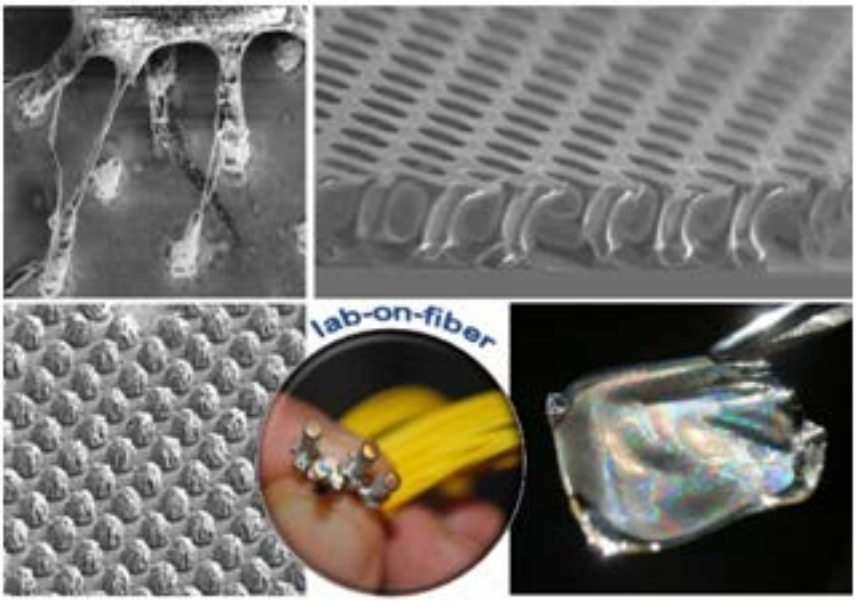
Le superfici nanostrutturate possono offrire diversi vantaggi rispetto a quelle flat in termini di interazione con il mezzo esterno (interfacce), di interazione con molecole o biomolecole (inclusione) o di interazione con la luce. Proprio come succede in natura, la nano strutturazione permette di ottenere proprietà quali la non-bagnabilità, l'autopulizia, l'antiriflesso o l'iridescenza, che non sono determinate direttamente dalla composizione chimica dei materiali ma dalla loro organizzazione morfologica. Al POP-Lab di Milano si sviluppano superfici nanostrutturate polimeriche o organiche ad alto grado di definizione, utilizzando tecnologie a basso costo che non richiedono l'impiego di strumentazione tecnologicamente avanzata. Le tecniche utilizzate, prevalentemente basate su self-assembly e su soft-litografia, permettono di svulippare materiali con proprietà utili in diversi campi dell'optoelettronica, dai dispositivi per emissione di luce fino al fotovoltaico e ai biosensori.



Parole chiave: antireflective, biomimetic, self-assembly, nanosphere lithography, sensors, OLED, solar cells

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Functional Organic Field-Effect Transistors: From the Realization of Bright Nanoscale Light Sources to the Implementation in the Stimulation and Sensing of Living Systems

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Functional organic field-effect transistors (OFETs) have attracted increasing attention in the past few years due to their wide variety of potential applications such as in light detection, signal storage, laser emission, environmental monitoring and medical diagnostics, which are all highly important in modern society.
In the first part of the invited talk, I introduce ambipolar organic light-emitting transistor as a highly integrated multifunctional optoelectronic device whose photonic features are modulated in terms of emitted optical power, color coordinates and angular emission profiles by integrating a transparent oxide photonic crystals as a gate dielectric. The engineering of the integrated photonic device results in the enhancement of the emitted-power and brightness by x5- and x13-factors, respectively [1].
In the second part of the talk, I will introduce the Water-Gated Organic Field-Effect Transistor (WGOFET) as one of the most promising device architectures for stimulating and recording cell electrophysiological activity [2]. In particular, I will present for the first time the use of two electron-transporting PDI derivatives, named PDIF-CN2 and PDI8-CN2, as active materials in WGOFETs. The two materials have identical solid-state arrangement but show two different growth mechanisms: almost-2D layer-by-layer for PDIF-CN2 and 3D for PDI8-CN2. Moreover, PDIF-CN2 shows one-order-of-magnitude higher mobility in WGOFET configuration. By cross-correlating experimental and theoretical evidences, we suggest that the charge-mobility increase in PDIF-CN2 is likely correlated to a bulk-dependant contribution to the field-effect charge transport. Moreover, we also propose and experimentally validate a new circuital model for describing the ionic charge accumulation and flux at the region at the boundary between the physiological solution and the organic layer in an electrolytic two-electrode vertical device structure.

Parole chiave: multifunctionality, field-effect transistors, water-gate, photonic, light-emission, brightness, morphology-performance correlation

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Charge Transport Behavior of Reduced Graphene Oxide: Understanding the Mechanism From Single Sheet to Thin Film

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Graphene is one of the most promising new materials and is attracting a great deal of interest because of its outstanding properties. Such unique characteristics have led to various graphene-based materials (GBMs) being produced for applications in diverse technological fields including (opto)electronics, photonics, as well as energy generation and storage.

We focus on the study of graphene oxide (GO) and its graphene derivative as a model material system for defining quantitative approaches to describe GBMs, due to its morphology and high-processability. Using strong oxidation procedures in liquid, suspensions of monoatomic layers were prepared in water and shown to be stable over several years.

In general, several detailed studies on the charge transport properties have been performed for single RGO [1-4] sheets while less work has been devoted to thin films and so a systematic study is still lacking [5-8]. Most studies give an ambiguous interpretation of charge transport phenomena by qualitative plot of resistance vs temperature, while a univocal interpretation of the charge transport phenomenon is still object of debate: Efros-Shklovskii variable-range hopping (ES-VRH) or 2D Mott variable-range hopping (2D-VRH).

We attempt to perform a quantitative study of the charge transport properties of such GBMs. The chemical composition, film thickness and the lateral size of single layers were monitored quantitatively providing detailed analyses of charge transport properties of RGO thin films. We report a systematic data analysis and modelling of experimental data of the resistance of RGO thin films of different thicknesses (figure 1). Such films are described as multi-layered networks where hopping events affect the in-plane charge transport whereas out-of-plane transport is quasi-metallic. Based on analysis of the reduced activation energy W(T) [9], we show that the charge transport mechanisms strongly depend on hopping events, following different regimes at different temperatures: ES-VRH between 10-100°K and power-law at 100-250°K [10] .

Moreover, we further correlate the electronic transport mechanisms with the morphology of the RGO film (figure 2). The probability that charges can circumvent the hopping barriers increases with film thickness, with a corresponding increase in the effective delocalization of the electronic states up to the micron scale.

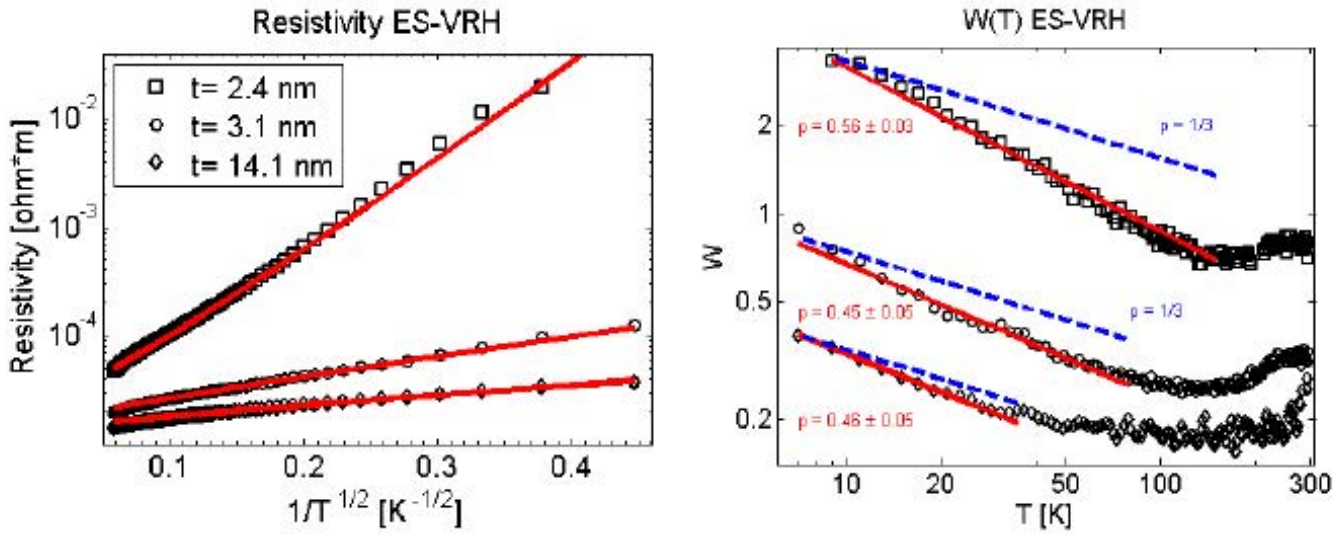

Figure 1. right: Resistivity of the RGO thin film vs $T^{-1/2}$ fitted with ES-VRH, showed for 3 different thicknesses (2.4 nm, 3.1 nm, 14.1 nm). Left: Reduced activation energy (W) obtained from the resistivity measured at 3 different thicknesses (2.4 nm, 3.1 nm, 14.1 nm). The charge transport at low temperature can be univocally associated to ES-VRH (p=1/2).

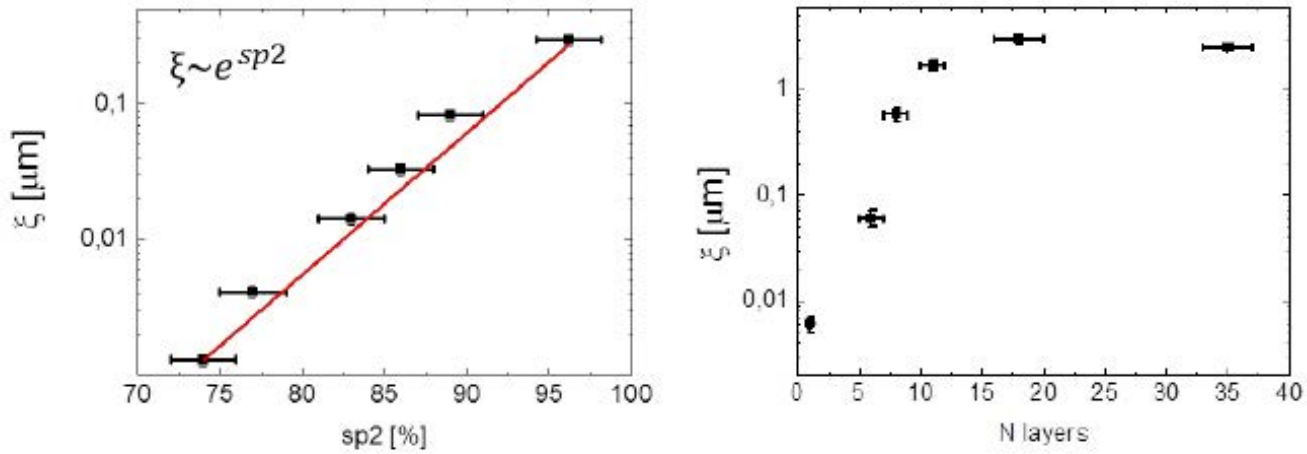

Figure 2. right: exponential behavior of the localization length (ξ) of the electronic states vs sp2 extension. Left: saturation of the localization length (ξ) vs number of RGO single sheet layers in the thin film.

Parole chiave: Reduced Graphene Oxide, Charge transport, Efros Shklovskii Variable Range Hopping, Reduced Activation Energy

Ringraziamenti:
Graphene Flagship 696656

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Multifunctional Smart Ceramic Materials: Ferroelectrics/ Piezoelectrics

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Intelligent materials, with one or more properties that can be modulated by external stimuli (mechanical stress, electric or magnetic field), are used in domotics, mechatronics, medical, security, portable devices, communications etc. Through a multidisciplinary approach and the design of innovative micro-nano-structures, several functions are combined in the same structure. The study is aimed at: i) materials with specific compositions for structural, dielectric and anelastic characterization for basic studies (coexistence of phases or defect movements, etc.), ii) piezoelectric materials for application in miniature wearable devices, III) engineered multi-functional structures of piezoelectric, conductive and magnetic (multiferroic) materials with different architectures (particulate, layered, compositional gradients etc), IV) process development related to the scale up (reliability of performance and reproducibility), V) study of materials for application in wearable devices. Examples will be shown of the running research projects related to a) phase analysis of PZT based materials at the ferroelectric/antiferroelectrc transition, b) enhanced properties of multiferroic composites by new approach to conventional ceramic processing techniques.

Parole chiave: Ceramic processing, piezoelectrics, ferrite, microstructure.

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MODELLING COMPUTAZIONALE

COMUNICAZIONE ORALE

Il Modelling e l'Industria: Due Esperienze Positive

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Il modeling, specialmente a livello ab-initio, molto spesso è percepito come lontano dalla complessità sperimentale, a cuasa delle limitazioni di scala spaziale e temporale.
In questa presentazione, illustrerò due casi in cui il modeling ab-inito ha permesso di risolvere problemi di grande importanza tecnologica, in collaborazione con due partner industriali: il breakdown dell'isolamento elettrico nei cavi coassiali soggetti ad altissimo voltaggio (Pirelli Cavi e Sistemi) e il problema della degradazione (*roll off*) di emettitori OLED nel blu (in collaborazione con Samsung).
Infine, mostrerò come le tecniche computazionali, alcune delle quali sviluppate anche all'ISTM, ci permettono di comprendere e modellizzare materiali e sistemi complessi come il cemento, nuove batterie a litio, e dispositivi microelettronici basati sulla spintronica.

Parole chiave: Density Functional Theory, dinamica molecolare, polietilene, organic LED, cemento, grafene, batterie al litio, spintronica

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First-principle Modeling of the Catalytic and Optical Properties of Metal (Ultra) NanoStructures

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I will present an overview of theoretical methods, concepts and applications in the field of metal (ultra) nanostructures, with focus on catalytic and optical properties and paying specific attention to quantum mechanical approaches and modeling of realistic conditions.
Starting from methods for systematic sampling the compositional and structural degrees of freedom, I will briefly discuss a Reactive Glocal Optimization (RGO) approach as a computational protocol able to explore the reactive phase space of these systems in the presence of reactant molecule [1], from elemental diffusion in alloyed systems [2] to heterogeneous catalysis [3-5]. RGO will be framed within the topic of the long-term structural dynamics of kinetics-driven off-lattice activated processes. I will then show how the application of RGO under realistic conditions naturally leads to the concept of ligand/surface catalytic complex, i.e., a complex aggregate formed *in-situ* by metal catalyst, support, and ligands at various stages of the reaction, which acts as the real catalytically active species (with ligand/ligand interactions and catalyst restructuring playing a decisive role). I will finally present selected examples of key heterogeneous catalytic processes: CO oxidation to CO_2, CO_2 reduction reaction, oxygen reduction reaction (ORR) [6], N_2 hydrogenation (Haber-Bosch), all dealing with the activation of small molecules, and ranging from solid/gas to solid/liquid (electro-chemical) interfaces, and from the ultranano to the nano régime, with the underlying theme of linking fundamental understanding to catalyst design and optimization.
Moving to electron dynamics, the absorption spectra of metal nanoclusters will be explored using time-dependent density-functional-theory (TDDFT) methods. Attention will be focused on the field of monolayer-protected clusters (MPC), whose atomistic-level definition lends itself to stringent match between theory and experiment, and which have potential applications in molecule detection via Raman spectroscopy, enhanced plasmonic phenomena in metal nanogaps, biosensing, etc. The sensitivity of Surface Plasmon Resonances (SPR) [7] to the nanostructure environment and the effect of ligand species will be investigated. It will be shown how to use molecule/nanostructure resonance coupled with plasmon/plasmon interactions due to proximity effects (synergic interactions in the optical response or 'hot-spot' enhancement of response fields) [8] and/or fine tuning of the chemical features of the ligands (steric hindrance and delocalization via π-conjugation to achieve optimal band alignment) [9] to achieve large enhancements in absorption intensity in the near-IR/vis region (SPR "re-birth"). This will be coupled with an analytic understanding of the MPC building principles [10], a step forward toward the goal of *in-silico* design of metal (ultra)nanostructures with desired optical properties.

Parole chiave: heterogeneous catalysis, plasmon resonance, reactive sampling, oxygen reduction reaction, Haber-Bosch

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Melting and Sintering of Si Nanoparticles by Molecular Dynamics Simulations

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Nanomaterials nowadays are widely applied in different technological fields and the interest in their large-scale production has grown accordingly. Si nanoparticles (NP), in particular, are considered to have a great potential for device developments in the semiconductor and photovoltaic industry. The bottom-up synthesis from the gaseous phase is particularly attractive because, avoiding the use of solvents, is generally considered more ecological and suitable for large-scale production. Synthesis from low temperature plasma begins to be used at industrial level, but the optimization of the production process for a synthesis aimed at the formation of well defined NP is still an open problem. In the bottom-up synthesis process, the very basic bricks in the reactor are in general the individual atoms that end up forming NP through several concurrent processes such as nucleation, atomic deposition, aggregation, coagulation, sintering, coalescence, chemical reactivity, which occurs in the early stages of the synthesis process. Obtaining experimental information on the processes occurring in the plasma reactor at temperatures of thousands of degrees is rather complicated.
We are currently engaged [1,2] in the development of numerical models and procedures to simulate reactions, interactions and characterize dynamically, at the atomic level, the various phases that determine the formation of nanomaterial aggregates in the environment of a plasma reactor. The aim is the understanding of the basic processes and the definition of specific parameters and mathematical expressions for a realistic parametrization of a computational model at the mesoscale level where bigger systems and their dynamics can be simulated in detail on a larger spatial and time scale.
Preliminary results of our numerical modelling of the melting and sintering/coalescence of Si clusters with dimensions in the range of hundreds of atoms will be presented by the present talk. This kind of information is crucial for understanding the dynamical processes of nucleation and growth and the relative stability of the Si clusters of different dimensions that are present in the plasma reactor in order to optimize the selective synthesis of NP with specific features.

Parole chiave: Si nanoparticles, atomistic simulation, molecular dynamics, melting, sintering
[1] DOI 10.3390/cryst7020054
[2] DOI 10.1021/acs.jctc.

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BENI CULTURALI

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Smart and Sustainable Approaches for theReliable and Long-Lasting Conservation of Metal Works of Art

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The degradation processes in Cultural Heritage artefacts represents a critical issue since they can irreversibly compromise the conservation status of valuable works of art and modify the surface appearance leading to the formation of alteration products and reactive compounds. Many approaches have been developed for the protection and conservation of metal artefacts, mainly based on passive coatings with barrier properties for external aggressive species and usually toxic corrosion inhibitors that chemically stabilize the metal surface hindering the interaction with degrading agents. A particular attention has been payed to the occurrence of degradation processes in copper-based works of art, with special emphasis for chloride-induced processes. These latter are extremely harmful for copper-based alloys since are responsible for the "bronze disease", a cyclic copper corrosion process that can continuously transform the alloy in a greenish powder of copper hydroxychloride polymorphs, such as atacamite.
At present, concerns related to the degradation of both ancient and modern copper-based works of art are still relevant and the most effective protective materials are commonly based on the use of toxic corrosion inhibitors and large amounts of harmful organic solvents for their application and removal. Therefore, innovative approaches to fulfil the protective, aesthetic and safety requirements are demanding.
In this context, we have focused our attention on the development of smart nanostructured polymer coatings able to provide an active protection of copper-based works of art and easy to be applied and removed by using not toxic solvents (i.e. water and ethanol). We prepared these innovative coatings by using stimuli responsive nanoparticles embedded into a polymer matrix consisting of environmentally friendly polymers from renewable sources, such as chitosan, alone or in blends. The research activities are carried out within the H2020 Nanorestart "NANOmaterials for the REStoration of works of ART" project and are aimed to the safe, reliable and long-lasting protection of modern artifacts. The first applications of chitosan-based coatings on works of art in collaboration with Peggy Guggenheim conservators have provided very positive feedbacks due to their superior protective and aesthetic properties, and high safety with respect to commercial benchmarks.
Based on these findings, smart approaches for the inhibition of degradation processes will be also applied to the protection of steel rebar in concrete monuments in the framework of InnovaConcrete "Innovative materials and techniques for the conservation of 20th century concrete-based cultural heritage" project, recently founded by the European Commission.

Parole chiave: Smart materials; Active coatings; Sustainable conservation; Metal works of art.

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Pigment-Oil interactions in Paintings: Nature and Distribution of Metal Soaps by FTIR Spectroscopy

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Formation of metal carboxylates (metal soaps), originating from the interaction of certain metal ions contained in pigments (mostly Zn, Pb and Cu) with the free fatty acids produced by hydrolysis of triglycerides in the oil binding medium, is a crescent concern in painting conservation. Metal soaps, in fact, may expand, aggregates and migrate within the paint layer causing severe aesthetical and mechanical damage to the painting, being protrusions, efflorescence, delamination, pitting, and increasing transparency the most dramatic effects. Despite the widespread occurrence of these phenomena and the growing interest of the scientific community in this topic, the process of formation and evolution of metal soaps in oil paintings is not yet fully understood. Within the transnational access activity of MOLAB, the nature and distribution of metal carboxylates have been non-invasively characterised by reflection mid-FTIR spectroscopy in a large number of ancient and modern artworks, significant to draw some general considerations about the forms and the extent by which metal soaps manifest on painting surfaces. In support of the non-invasive study, a systematic investigation of artificially aged oil model paintings has been carried out. The reactivity of various pigments in the oily medium, the roles of paint additives, and the evolution and localization of different forms of soap aggregates within the paint layer, have been closely investigated by combining reflection, transmission FTIR and (ATR)–FTIR imaging. As an example of the outcomes of this broad research, the state of conservation the iconic painting *Alchemy* by J. Pollock (1947, Peggy Guggenheim Collection, Venice) was monitored at the macro and micro-scale revealing the underlying mechanism of Zn-soap formation before the appearance of any aesthetical or mechanical effects and thus providing a valuable warning bell for the conservators.

Parole chiave: oil paintings, metal soaps; reflection FTIR spectroscopy, micro FTIR imaging.

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CHIMICA VERDE

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Synthesis of Benzyltriazolyl-BOX Ligands and their Application in the Asymmetric Copper(II) Catalysed Nitroaldol Reaction

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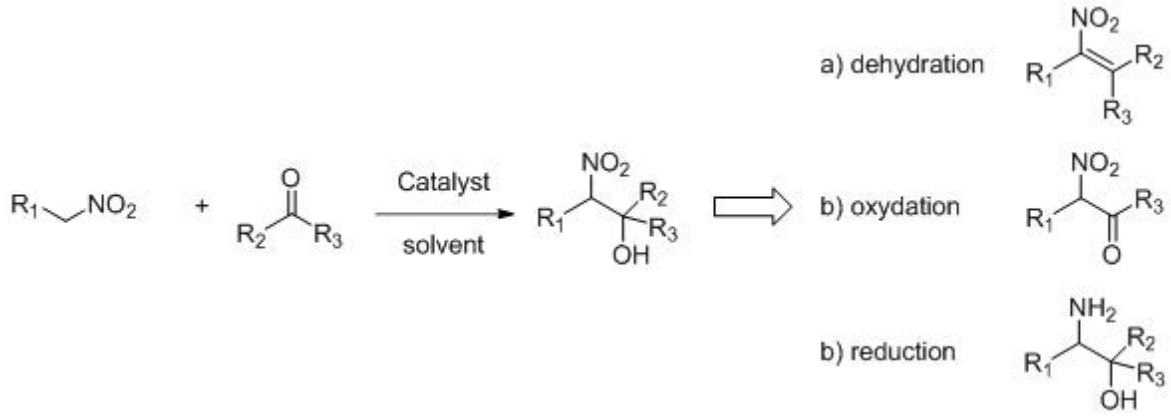
The Henry reaction (also known as nitroaldol reaction) is a base catalysed C-C bond-forming reaction between nitroalkanes and aldehydes or ketones. The reaction leads to β-nitroalcohols that are widely used intermediates in organic synthesis due to their versatility (see scheme 1).



Scheme 1: Potential application of the Henry reaction in organic synthesis.

The Henry reaction can also be catalysed by several metal complexes such as Cu, Zn, Co, Cr, Pd, and rare metals. Of particular interest is the asymmetric version of the reaction. In this contest, Cu(I)- and Cu(II)-complexes are often used because of their availability and low toxicity. Moreover, copper possesses excellent chelating properties and allows the coordination of bidentate as well as polydentate ligands. The first example of copper catalysed asymmetric Henry reaction was reported by Jørgensen in 2001 by applying bisoxazoline ligands.[a] Since then several different nitrogen-based ligands such as bisoxazolidines, diamines, (−)-sparteine, sulfonyldiamines, sulfonimidamides, tetrahydrosalens and N,N'-dioxides have been reported.
In line with our recent interest in the synthesis of nitrogen based ligands and their application in metal catalysed asymmetric reactions[b] we wish to report about the synthesis of new benzyltriazolyl-bis(oxazoline) ligands with some preliminary result in the addition of nitromethane to substituted benzaldehydes.

Parole chiave:
Henry reaction, enantioselective catalysis, copper complexes, BOX-ligand

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La tirosinasi [EC 1.14.18.1] è un enzima, contenente rame, coinvolto nella biosintesi della melanina, nell'indesiderato imbrunimento enzimatico di alimenti di origine vegetale, nella melanogenesi patologica e nei fenomeni di muta degli insetti [1]. La tirosinasi catalizza l'ossidazione sia dei monofenoli (attività monofenolasica o cresolasica) che degli o-difenoli (attività difenolasica o catecolasica) a *o*-chinoni, pertanto la ricerca di nuovi inibitori della tirosinasi può portare allo sviluppo di nuovi agenti per lo sbiancamento della pelle, a nuovi farmaci e composti per il controllo degli insetti nocivi [2]. I bifenili idrossilati sono una classe di polifenoli ampiamente presenti in natura [3], alcuni di essi manifestano una elevata attività biologica come ad esempio gli ellagitannini, la vancomicina e le bifenomicine. E' noto come i bifenili manifestino una maggiore attività antiossidante e siano generalmente meno tossici dei corrispondenti monomeri [4]. Nel ambito delle nostre ricerche riguardanti la sintesi di bifenili idrossilati con interessanti caratteristiche stereochemiche e biologiche [4], abbiamo preparato una piccola collezione di bifenili idrossilati a simmetria C_2 e abbiamo valutato la loro capacità di agire da inibitori della tirosinasi utilizzando sia metodi spettrofotometrici che elettrochimici. I risultati ottenuti con entrambi i metodi sono risultati comparabili. La maggior parte dei composti hanno dimostrato una maggiore attività inibitoria rispetto al 4,4'-diidrossibifenile, un noto inibitore di tirosinasi. I nostri risultati suggeriscono che i bifenili idrossilati costituiscono una promettente classe di composti per lo sviluppo di nuovi inibitori dell'enzima tirosinasi.

Parole chiave: Bifenili idrossilati, enzima tirosinasi, sintesi.

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Exploiting the Distal Reactivity of Indolyl Methylenemalononitriles: An Asymmetric Organocatalyzed [4+2] Cycloaddition with Enals Enables the Assembly of Elusive Dihydrocarbazoles

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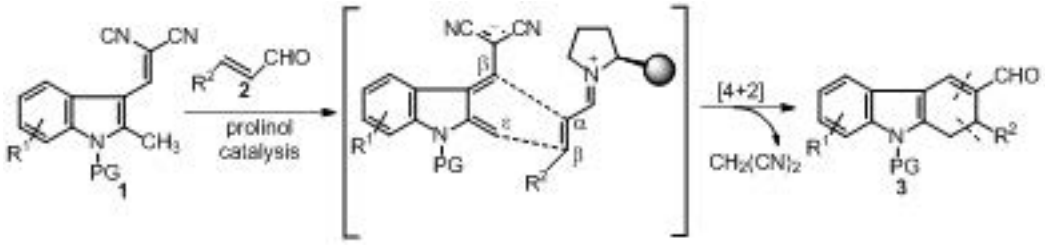
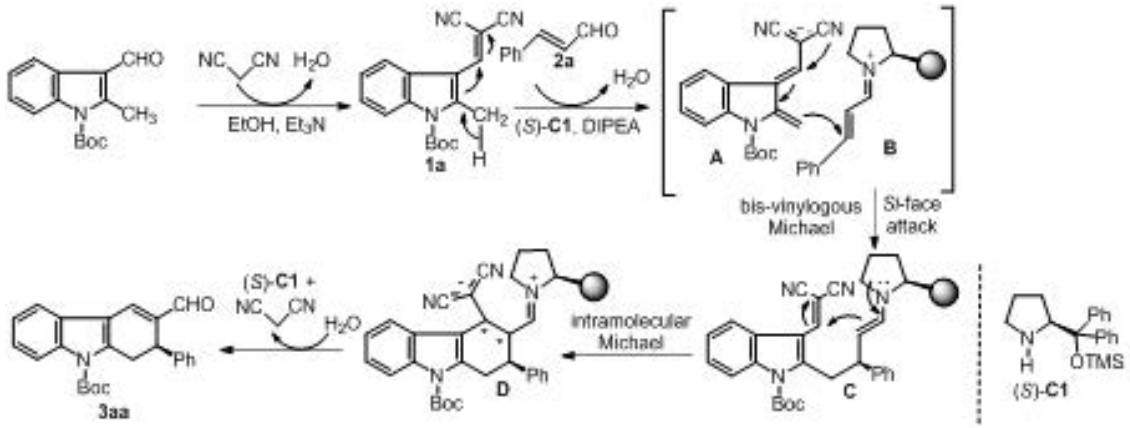
Polycyclic indole architectures, including carbazole and hydrocarbazole skeletons, represent privileged structural motifs found in a number of natural alkaloids, many of which displaying interesting activities against a diverse set of biological targets.[1] Accordingly, the search for efficient methods for the assembly of these structures has drawn a great deal of attention in the synthetic organic chemistry community.[2,3] An unprecedented technique for the in situ generation of indolyl *ortho*-quinodimethanes from 2-methylindole-based methylenemalononitriles **1** by amine-mediated remote C(sp^3)-H deprotonation was developed. These intermediates were efficiently trapped by diverse enals to provide a rapid entry to 2,9-dihydro-1*H*-carbazole-3-carboxyaldehyde structures **3** through a formal asymmetric [4+2] eliminative cycloaddition governed by a α,α-diphenylprolinol trimethylsilyl ether catalyst.[4]



A stepwise reaction mechanism of the formal catalytic asymmetric [4+2] cycloaddition of methylenemalononitrile **1a** with enal **2a** catalyzed by (*S*)-**C1** is proposed.



Parole chiave: asymmetric synthesis, cycloaddition heterocycles, organocatalysis, vinylogy

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Low Electro-Polymerization Potentials of Natural Phenols Can Improve Sensing Performances of Derived Films

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Often first-generation amperometric biosensor designs are based on Red-Ox reactions that commonly generate H_2O_2. Unfortunately, at this potential other naturally occurring molecules such as ascorbic acid (AA) or dopamine (DA) can be oxidized. Phenylendiamines (PPD) are commonly used to avoid this problem: when these compounds are electro-deposited on the transducer surface, a highly selective membrane is formed1. Unfortunately PPD monomers are considered carcinogenic. Aim of this work was to evaluate the suitability of natural phenols as non-toxic alternatives to the *ortho* isomer of PPD. The electro-synthesis over Pt-Ir electrodes of natural 2-methoxy phenols such as guaiacol, eugenol and isoeugenol, and hydroxylated biphenyls like dehydrodieugenol and magnolol were fully assessed. They showed quite good values of permselectivity for biosensor application, but not as good as PPDs[3]. In order to improve permselectivity of films several electro-polymerization potentials were applied by means of constant potential amperometry[4]. The electro-polymerization potentials used are significantly lower than values commonly applied and better permselective properties were obtained. The electrodes coated with phenols were stable and responsive throughout two weeks. Among the tested compounds, *iso*eugenol and magnolol proved as permselective as poly-*ortho*-PPD and may be considered as effective polymeric alternatives. Also a biosensor based on acetylcholine esterase and choline oxidase enzymes was electro-coated with a poly-magnolol film in order to prove feasibility of this newly electro-synthetized films in a first generation amperometric biosensor.

Key words: biosensors, electrodeposition, magnolol, permeability, permselectivity.

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Metal/Acid Bifunctional Catalyst for the One-Pot Conversion of Sugars into High-Added Value Chemicals

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1. Scope

The depletion of fossil resources has compelled the scientific community to seek alternative raw materials for the production of platform and high-added value molecules and to develop appropriate and sustainable conversion technologies. In the present work, we report the selective, direct conversion of concentrated water solutions of glucose and xylose into the corresponding dehydration sugars alcohols using a novel resin-supported bifunctional catalyst.

2. Results and discussion

The catalyst 0.2 wt% Ru@Dowex-H was prepared by immobilization of RuNPs of 1.3±0.5 nm onto commercial gel-type acidic Dowex-50WX2 resin. The catalyst showed to be truly bifunctional since it catalyzed the one-pot conversion of glucose into isosorbide through a first hydrogenation step to sorbitol followed by a two acid catalyzed dehydrations via 1,4-sorbitan. Isosorbide was obtained with 85% selectivity at full conversion under 30 bar H2 and 190°C. In addition, by tuning the reaction conditions (120°C), the same catalytic system produced sorbitol with 99.9% selectivity at full conversion. Isosorbide finds application in the cosmetic, pharmaceutical and bio-based plastic industries and sorbitol is largely used in the food and also pharmaceutical industries.

Similarly, one-stage catalytic conversion of xylose proceeded through fast hydrogenation to xylitol, followed by selective dehydration to give 1,4-anhydro-D-sorbitol with 94.9% yield at 190°C and 30 bar H2. Besides, the reaction at lower temperature (120°C) gave quantitatively the hydrogenation product xylitol, which is used as sweetener and refreshing agent in foods and toothpastes.

To the best of our knowledge, the proposed catalyst is the first example reported for both the direct catalytic conversion of glucose into isosorbide with high yield, and the synthesis of 1,4-anhydro-D-xylitol in one-pot, one-stage.

3. Conclusions

A heterogeneous bifunctional catalyst comprising 0.2 wt% ruthenium onto a Brønsted acid solid support achieved in one-pot the selective multi-step conversion of lignocellulose-derived monosaccharides to fine-chemicals. The anhydro-sugar alcohols of glucose and xylose were obtained with 86% and 95% yield, respectively.

Parole chiave: bifunctional catalysts, one-pot reactions, lignocellulosic biomass P. Barbaro, F. Liguori, C. Moreno-Marrodan, Green Chem., 2016, 18, 2935-2940.

A Step Forward from PTA: Ru-Arene Complexes of CAP Ligand as Promising *in vitro* Anticancer Agents

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For several years, the interest of our research group focused on the synthesis and coordination properties of the neutral water-soluble aminophosphine PTA (1,3,5-triaza-7-phosphadamantane, Figure 1 left) and its derivatives.[1] In our laboratories, some PTA transition metal complexes were successfully employed as catalysts for water-phase hydrogenations and hydroformylations, and their use as anticancer agents in medicinal inorganic chemistry was also demonstrated.
Recently, a higher homologue of PTA, namely ligand 1,4,7-triaza-9-phosphatricyclo[5.3.2.1]tridecane (CAP, Figure 1 right), was reported in the literature.2 With the aim of exploring its coordination ability and properties, we obtained and characterized three novel ruthenium(II)-arene half-sandwich complexes bearing CAP as monodentate ligand. The new Ru(II)-CAP complexes (RACAP) showed modest activity in homogenous C=C bond catalytic reduction tests. On the other hand, when tested in vitro against selected cancer cell lines, they revealed higher activity than the corresponding well-known PTA analogues (RAPTA), still exhibiting a reasonable degree of cancer cell selectivity.[3]

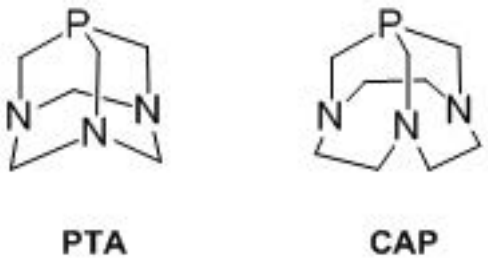

Figure 1.

Parole chiave: water-soluble phosphines; arene ruthenium complexes; anticancer agents.

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Catalysis by Group IV Amido-Pyridinate Complexes for the Reduction of Carbon Dioxide to Methane

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A highly attractive renewable energy technology involves the transformation of CO_2 into fuel. Indeed, CO_2 has not to be regarded as a waste product from the combustion of fossil fuel but rather as a chemical resource to be harvested and recycled into products of added value using the assistance of a catalyst. The metal-mediated CO_2 reduction with silanes (hydrosilylation) is a thermodynamically favored chemical process and it can be conveniently applied to the transformation of this feedstock. Early transition-metal complexes stabilized by nitrogen-containing ligands have been identified as valuable candidates for a number of highly efficient and selective catalytic transformations (1). In particular, amidopyridinate Group-IV organometallics have shown excellent performance as catalysts precursors in olefins oligomerization, polymerization, and copolymerization (1,2) as well as in the intramolecular hydroamination of primary and secondary aminoalkenes (2). In search for catalytic applications in the renewable energy field, we have focused on a new class of neutral dibenzyl Zr ^{IV} and Hf ^{IV} complexes stabilized by a tridentate dianionic benzoimidazolyl-amidopyridinate ligand [$(N^-,N,N^-)M^{IV}Bn_2$; M = Zr, Hf] as pre-catalysts for the CO_2 hydrosylilation reaction.(3) In this study, we have demonstrated that their in-situ activation with an equimolar amount of $B(C_6F_5)_3$ leads to the generation of cationic monoalkyl species. In the presence of silanes, these cations promote the CO_2 reduction to methane under mild reaction conditions (room temperature and 1 atm of CO_2). ^{13}C- and $^{13}C\{^1H\}$-NMR experiments with isotopically enriched $^{13}CO_2$ have been conducted to check the reaction course through the generation and conversion of all the reduction intermediates. A full account of the catalytic performance of these Group IV amido-pyridinate complexes in the reduction of carbon dioxide with various hydrosilanes will be discussed.

Parole chiave: water-soluble phosphines; arene ruthenium complexes; anticancer agents.

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La conversione della biomassa lignocellulosica in biocarburanti o bio–prodotti mediante idrolisi enzimatica richiede quattro fasi principali: pretrattamento, idrolisi, fermentazione e recupero finale del prodotto desiderato. La produttività e la fattibilità economica di tutto il processo dipendono da tutte e quattro le fasi, ma l'idrolisi enzimatica è riconosciuta come la più importante. La reazione enzimatica è influenzata da diversi fattori, come la fonte della biomassa (composizione in lignina e polisaccaridi), la natura degli enzimi coinvolti (cellulasi, glucosidasi e enzimi ausiliari) e infine le condizioni operative (pH, tampone e carico).
Le ricerche hanno mostrato che nel pretrattamento organosolv (OS) parametri diversi quali il tempo di reazione, la concentrazione e la natura del solvente e catalizzatore influenzano la composizione chimica della biomassa risultante, andando a condizionare la suscettibilità all'idrolisi enzimatica della cellulosa.
La canapa è una pianta industriale che produce fibre, semi e olio. La biomassa residua, il canapulo, è una biomassa di scarto interessante e può essere soggetta alla produzione di monosaccaridi. Si sono valutati per il pretrattamento OS la concentrazione del catalizzatore (H_2SO_4, 0-3% w/w), il carico (w/v), la temperatura e il tempo di reazione, che ne determinano la severità del processo (CSF). La dissoluzione della biomassa è funzione del CSF, influenzando così la composizione chimica dei solidi residui. Vengono prodotti tre –*streams*– legati alla produzione di lignina, xilani (*stream* C5) e cellulosa come solido residuo. L'idrolisi enzimatica del solido residuo è stata eseguita utilizzando la miscela di enzimi industriali Cellic® CTec (Novozymes). A 20 FPU/g e 10% del carico solido, porta ad una concentrazione di glucani (stream C6) fino a ~30 g/L con una produzione in glucosio di 0,44 g/gODW di biomassa pretrattata. Viene mostrata la correlazione tra pretrattamento OS e resa del processo enzimatico.
Come esempio di sfruttamento della componente zuccherina gli stream C5 e C6 sono stati fermentati ad un bio–prodotto di interesse industriale, l'acido L–(+)–lattico. Questo acido può essere utilizzato nel campo alimentare o come monomero per la preparazione polimeri biodegradabili (PLA, PLGA). Gli stream C5 e stream C6 sono stati fermentati separatamente ad acido L–(+)–lattico ad opera di Bacillus coagulans in condizioni di terreno povero, temperature elevate e in condizioni non sterili, con un eccesso enantiomerico oltre il 99% e una resa di 0,95 e 0,99 g/g con una produzione complessiva di 0,42 g/g di canapulo.

Parole chiave: biomassa lignocellulosica, pretrattamento, idrolisi enzimatica, fermentazione

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Modifiche Sintetiche di Composti Naturali Biologicamente Attivi

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La tematica svolta dal gruppo di sintetisti dell'ICRM si focalizza sulla preparazione di composti naturali biologicamente attivi. Attraverso competenze di chimica organica di sintesi e metodi di sintesi industriali, di sintesi asimmetrica (preparazione stereoselettiva di sostanze biologicamente attive, sintesi peptidica con amminoacidi sinteticamente modificati, modifica chimica di polimeri di origine naturale), di biocatalisi (trasformazioni enantio- e/o diastereoselettive, uso di enzimi idrolitici per la risoluzione di composti racemi e/o uso di enzimi isolati in reazioni di ossidoriduzione), di biotrasformazioni applicate alla sintesi (uso di microorganismi in reazioni di ossidoriduzione), di sintesi combinatoriale sono stati sviluppati numerosi filoni sintetici. Le principali classi di composti naturali biologicamente attivi studiate negli ultimi anni riguardano i sesquiterpeni a scheletro bisabolanico, attivi come antibatterici ed antitumorali, i sesqui- e diterpeni a scheletro monociclofarnesanico, gli apocarotenoidi (iononi, damasconi e derivati), aromi e fragranze appartenenti a differenti classi strutturali (mono- e sesquiterpeni, apocarotenoidi, eterocicli, lattoni), peptidi sinteticamente modificati (analoghi di Tubulisine) ad attività antitumorale, antibiotici a struttura amminoglicosidica con preparazione di una libreria di pseudo-pentasaccaridi modificati, poligalattomannani covalentemente legati ad analoghi chimicamente modificati di biocidi (BIT) allo scopo di aumentarne la "biostabilità", l'efficacia e l'emivita.

Verrà evidenziata la sintesi totale di Tubulisine e la loro applicazione nella terapia tumorale, la sintesi combinatoriale di composti coniugati alla struttura zuccherina della neomicina aventi proprietà antibatteriche, la sintesi stereoselettiva di aromi e fragranze (ambra grigia, iris e gelsomino) attraverso processi chemo-enzimatici, la sintesi di analoghi di BIT comunemente usati in formulazioni acquose ed il loro aggancio covalente a strutture poligalattomannaniche (ricavate da leguminose) tramite utilizzo di spacers e "click reaction".

Parole chiave: chimica organica, sintesi asimmetrica, biocatalisi, biotrasformazioni, sintesi combinatoriale, aromi, peptidi, polisaccaridi.

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New Eco Textiles From Agroindustrial Wastes: Valorization of Pineapple Leaves Fibres (PALF)

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The general definition of sustainable economy is the ability of an economy to maintain defined levels of economic production indefinitely. This theme is closely linked to the introduction of environmental friendly processes, to the study of new materials obtainable from renewable sources and to the exploitation and minimization of by-products and wastes from industrial processes. The biorefinery concept match all these aspects: in a biorefinery biomass conversion processes are integrated and value-added chemicals, new materials, fuels, power, heat, can be obtained in a sustainable way with environmental friendly processes. For this purpose the employ of enzymes play a key role in biorefineries because they constitute an important alternative to the traditional and environmental impact chemical compounds and processes [1].
An interesting example is the case of Thailand, where agriculture and textile industry are working together to exploit the resources obtainable from pineapple cultivation [2]. This nation produce over 2.2 million t/y of pineapple fruits; connected to this cultivation, recently, is developing a new business resulting from the extraction of fibers from leaves (PALF), to be employed in the textile sector.
These fibers are obtained from the leaves of the plant *Ananas Comosus*, which belongs to the *Bromeliaceae* family; they contain fibers (2.5 ÷ 3.5 %), pentosans (17.8 %), lignin (4.2 ÷ 12 %), fat and wax (3.3 %) and pectins (1.1 %) [3]. The presence of other constituents than fibers constitute an impurity that needs be removed, in particular lignin that act as a glue for the fibrillar structure of the fibers, is responsible of the non-wettability and consequently of the non-dyeing of the fibers.
This fiber is silky, fine and has interesting textile properties, is capable of blending with jute, cotton, ramie and some other synthetic fibres: so it can capture an important position among natural fibers as potential commercial grade textile fiber [4]. In consideration of its properties, PALF is placed between jute and cotton or jute and ramie. This work propose the development of an industrial process for extraction of fibres and exploitation of other constituents, in order to reach a sustainable and economical profitable production process.

Parole chiave: biorefinery, eco-textiles, pineapple leaf fibers, agroindustrial wastes.

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Innovative Green Routes to Noble Metal Nanoparticles

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The integration of green chemistry principles into nanoscience has attracted much attention over the past decade, aiming at the design of more sustainable synthesis processes. In this work, we report two environment-friendly and patented routes 1,2 to the production of different noble metal nanoparticles (Au, Ag, Cu, Pd) in form of stable suspensions even at high solid loading for application in catalysis 3-5 or as antibacterial coatings. In the light of the "green" synthetic strategy for industrial scale manufacture we exploited cheap, renewable and nontoxic reagents and water as solvet.
The first patented route is referred to surprisingly green and versatile synthesis of an innovative antibacterial hydrogel, based on AgNPs capped with hydroxylethylcellulose (Ag-HEC) and performed at room temperature. The outstanding potentialities of this method stem from its low toxicity and environmental impact combined with the absence of any kind of heating treatment and satisfying the typical industrial scale-up requirements. Spherical AgNPs of about 15-20 nm are prepared in form of concentered hydrogel suspensions (0.5-1%wt), stable over time (12 months), with tunable viscosity, outstanding antimicrobial activity (total bacterial depletion), but reduced cytotoxicity. With the same method also Au, Ag and Pd have been prepared. The easiness and the efficiency of the method represent a further advantage with respect to the common synthesis strategies.
The second patented route exploits glucose as non-toxic reducing agent, polyvinylpyrrolidone (PVP) as chelating additive and microwave as heating source to foster the homogeneity. By means of this preparation spherical bimetals (AuCu, AuAg, PdCu, AuPd) as well as the respective monometallic nanoparticles are synthesized in form of stable highly concentered (0.5-4%wt) suspensions. A deep characterization has been performed on prepared sols using HR-TEM, EDS, UV-vis spectra and XRD analysis. Thanks to an accurate reaction optimization particle size-control, total reaction yield and longtime stability (12 months) have been achieved. The so-prepared nanoparticles showed excellent catalytic properties, which have been tested in the reduction of 4-nitrophenol with NaBH4, as a probe reaction.

Keywords: Ag nanoparticles, eco-friendly synthesis, noble metals, catalysts

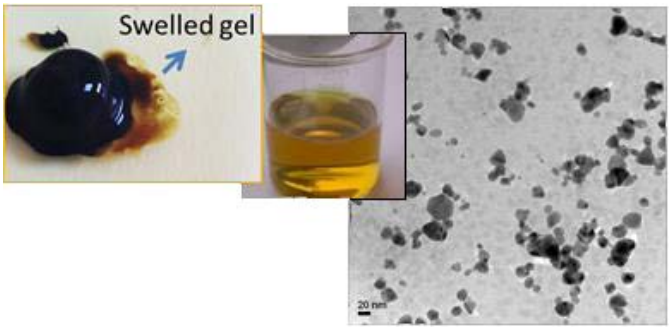

Fig 1- AgHEC in form of gel and Ag-Glucose. TEM analysis of AgHEC NPs

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Carbon Dioxide Hydrogenation Catalysed by Fe(II) and Mn(I) PNP Pincer Complexes

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The catalytic reduction of carbon dioxide is of great interest for its potential as hydrogen storage method and to use carbon dioxide as C-1 feedstock.[1] In particular, the selective reaction of molecular hydrogen with CO_2 offers the possibility to generate novel hydrogen carriers or fuels, such as formic acid, a widely studied target molecule as it provides access into the chemical as well as the energetic value chain.[1]
In an effort to replace expensive noble metal-based catalysts with cheaper, earth-abundant counterparts, we report the first example of Mn(I)-catalysed hydrogenation of CO_2 to HCOOH. The novel Mn(I) catalyst [Mn(PNP-iPr)(H)$(CO)_2$] supported by a PNP pincer ligand showed higher stability and activity than its Fe(II) analogue.[3,4] TONs up to 10000 and quantitative yields were obtained after 24 h using DBU as base. Further improvements showed that at catalyst loadings as low as 0.002 mol%, TONs greater than 30000 could be achieved in the presence of LiOTf as co-catalyst, among the highest activities reported for a non-noble metal catalyst for CO_2 hydrogenation to date.

Parole chiave: CO_2 utilisation; manganese; iron; homogeneous catalysis; pincer complexes.

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Hydrogen Generation by Electrochemical Reforming of Bioalcohols

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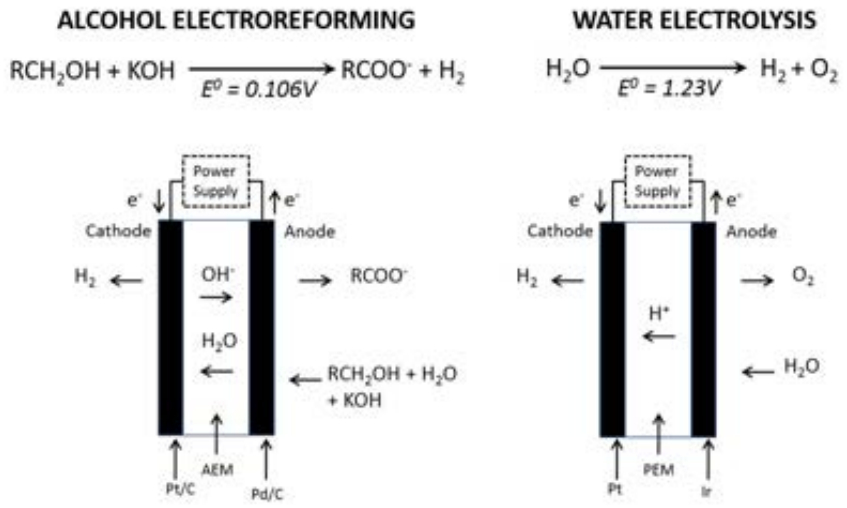
The production of hydrogen by the electrolysis of water is a well-established technology. However, it does not have a significant commercial impact due to its high-energy cost. A traditional Proton Exchange Membrane (PEM) electrolyzer needs more than 45 $kWhkgH_2^{-1}$ to achieve a significant rate of hydrogen production (1). This is the main reason why water electrolysis accounts for only a small proportion of the world's hydrogen production (circa 4%).

Since the thermodynamic barrier of water electrolysis consumes 68% of the whole energy input of the device, our strategy for reducing the energy cost is the replacement of the unfavorable anodic oxygen evolution reaction with a more suitable reaction: the partial oxidation of a bioalcohol to a carboxylate. This process needs only 20 kWh for the evolution of one kilogram of hydrogen at the same working conditions of traditional PEM electrolyzers, with a net energy saving of about 44%. Such electrolytic processes that lead to the concomitant generation of hydrogen and industrially relevant chemicals, like acetate and lactate, are often indicated as "electrochemical reforming", or "electroreforming" (2). In order to obtain selective oxidation of alcohols to carboxylic compounds of interest to the fine chemical industry, several anodic catalysts have been investigated, ranging from nanostructured palladium catalysts to rhodium organometallic compounds (1, 3).



Parole chiave: Hydrogen, Electroreforming, Biorefinery

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Multi-purpose Metal-Free Dyes for Energy and Hydrogen Production.

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Sunlight is, by far, the most abundant, economic and well distributed energy source over the world. For this reason, many different photovoltaic technologies exploit solar energy in order to produce electric current or eco-friendly fuels as hydrogen (1). Organic chemistry can play a pivotal role in the field of renewable energies because totally organic molecules are often the most suitable candidates as photoactive materials, thanks to their unique optical and electrochemical properties which can be finely tuned through a balanced modification of the structure of the compounds.
Our first interest in this field was the design and the synthesis of organic dyes as photoactive materials for Dye-Sensitized Solar Cells (DSSCs) (2), a very promising photovoltaic technology which is currently finding its market niche where the traditional silicon solar cells cannot be used. Recently we decided to broaden our horizons exploring new applications of our molecules toward other research fields which involve the exploitation of sunlight, such as in the photo-catalyzed production of hydrogen (3), or the employment of solid-state hole-transport materials (ss-HTMs) for DSSCs and PSCs (Perovskite Solar Cells) (4).
Our main interest was that of studying the influence of small structural modifications, such as the substitution of some functional groups or the insertion of alkyl chains in different regions of the molecules, on the physical and electrochemical properties of the dye, and on the efficiency of the final photovoltaic devices.

Parole chiave: Organic Chemistry, Photovoltaics, DSSCs, Hydrogen production.

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Studio dei Calori Specifici di Tetraedriti Termoelettriche

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Negli anni recenti le tetraedriti hanno visto un crescente interesse nell'ambito della ricerca sui materiali termoelettrci grazie alle loro promettenti proprietà. Uno degli aspetti promotori di questo interesse è la loro presenza nella crosta terrestre in forma di minerale, malgrado i processi di estrazione e purificazione siano complessi e spesso antieconomici. Tuttavia, un elevato numero di lavori è apparso in letteratura dedicato alla sintesi e caratterizzazione di questi materiali. Malgrado la crescente letteratura, una specifica analisi dedicata alla capacità termica, C_p, di questi materiali è ancora assente.
Tra le tecniche calorimetriche usate per la determinazione di Cp, la più diffusa è la differential scanning calorimetry (DSC), tecnica la cui precisione è sensibile a problemi di baseline. Rispetto alla DSC convenzionale, l'introduzione di una modulazione in temperatura (MDSC) può limitare significativamente sia aberrazioni di baseline, sia deviazioni ad alta temperatura, migliorando sensibilmente l'affidabilità dei risultati di Cp.
In questo lavoro verrà riportato lo studio eseguito sul Cp della tetraedrite termoelettrica $Cu_{10}Cu_{1-x}NiZn_xSb_4S_{13}$ con x = 0, 0.3, 0.5, 0.7 con la tecnica MDSC. Al fine di ottimizzare l'accuratezza dei risultati, sono stati condotti esperimenti a differente periodo di modulazione ma mantenendo l'ampiezza della modulazione lavorando in condizioni quasi-isoterme su un range di temperature tra 300K e 630K.

Parole chiave: Materiali per l'energia, Materiali termoelettrici, Analisi termiche

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Simultaneous Synthesis and Sintering of Tetrahedrite Based Material for Thermoelectric Application

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The interest in thermoelectric materials raised in the recent years due to the possibility to design thermoelectric generators (TEGs), reliable solid-state devices for waste heat recovery valuable in particular contexts where the employment of other technologies results inconvenient. Nowadays, the challenge in the thermoelectric field seems to be the identification of efficient thermoelectric materials, which should be also inexpensive, easy to synthesize, and comprised of earth-abundant elements.
On this basis, tetrahedrite mineral family (Cu12-xTrxSb4S13 where Tr= Mn, Fe, Co, Ni, Zn), one of the most widespread sulfosalts on Earth's crust, seems to meet the right features for an attractive sustainable p-Type Pb-free thermoelectric material showing relatively high conversion efficiency. The sulphide precursor powders were ball milled and then one-step simultaneous synthesis and sintering process was performed by open die pressing (ODP). By this simple, fast, and easy scalable route, thermoelectric pellets with a whole process lasting less than 6 hours. Both Zn and Ni cations were added as partial substituents of Cu in Cu12Sb4S13 permitting to considerably improve the thermoelectric performances of the undoped material prepared by ODP. The influence of precursors ratio on the tetrahedrite phase, secondary phase content and stoichiometry were investigated by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. The density and mechanical stability of samples were evaluated as a function of the chemical composition and processing parameters. A complete thermoelectric characterization was carried out for samples with different Zn and Ni substitution up to 400°C.

Parole chiave: tetrahedrite, thermoelectrics, Open Die Pressing, sintering

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Aqueous Processable Conjucated Polymers as a Green Tool for Optoeletronic Devices

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"Green materials" and "green" technologies are indispensable requirements to achieve the ambitious goal of sustainability in the field of electronics. In this context semiconducting organic materials that are low-cost and renewable hold great promise as environmentally safe alternatives to conventional inorganic counterpart. To this aim we have developed a new series of materials comprising a) a class of alcohol soluble materials based on π-conjugated backbones with pendant polar or ionic groups[1] for Interfacial engineering in optoelectronic devices and b) Rod-coil amphiphilic block copolymers for the preparation of water-processable NPs as active materials specifically for OPV.
The polar conjugated polymers (PCPs) have the typical properties of polymeric semiconductors, such as easy processability, chemical tunability, lightness and flexibility. Moreover, their alcohol solubility meets the growing demand for environmental friendly materials and allows for orthogonal solvent processability in all-solution-processed organic multilayer devices and their application as interfacial materials is an extremely promising way to potentiate the performances of organic electronic devices
We have explored the efficacy of a whole series of PCPs featuring a fluorene-based backbone with pendant phosphonate and/or amine groups as the cathode interfacial layer in three types of common optoelectronic devices□i.e. polymer based OLEDs,[2] colloidal quantum dot LEDs,[3] and polymer solar cells.
On the other hand we have developed a class of active materials for OPV based on Rod-coil amphiphilic block copolymers4 able to coordinate electron acceptors entities and can be used for the preparation of water-processable NPs through miniemulsion technique. The water-processable NPs showed a pre-aggregated morphology, with nano-areas (~10-20 nm comparable to exciton diffusion length) of the n-type and p-type materials and allow to get OPV cells which power conversion efficiency was around 75% of the ones obtained with the same materials processed using standard chlorinated solvent-based procedures. Moreover this methodology removes the necessity for non-conducting surfactants in the blend NP preparation, avoiding any additional purification step in the NP-OPV fabrication process.

Parole chiave: Conjugated Polymers, orthogonal solvents, aqueous processable, interfacial engineering, optoelectronic devices

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Effects of the Macrocyclic ligands in Copper(I) Pseudorotaxanes: Photophysics and NMR

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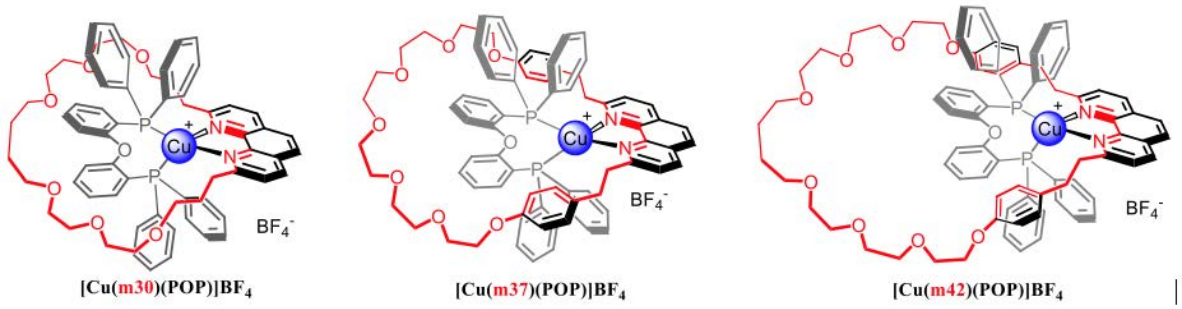
Heteroleptic Cu(I) complexes based on bis-phosphine (P^P) and 1,10-phenanthroline (N^N) ligands can be_designed to exhibit strong luminescence and, due to their relatively long excited state lifetimes and reducing character of the excited state, are used in photoredox catalysis.[1] $Cu(N^N)(P^P)]^+$ complexes are typically stable in solid but may undergo equilibration with related homoleptic structures in solution.[2] An effective strategy to overcome the formation of undesired homoleptic species in solution is the incorporation of the N^N ligand in a macrocycle, which can be threaded by the P^P ligand thus originating pseudorotaxane structures.[3,4] We have investigated three Cu(I) pseudorotaxane complexes based on a macrocyclic-ligand which includes a 2,9-substituted-1,10-phenanthroline chelator (N^N) and a bis[2-(diphenylphosphino)phenyl]ether (POP) ligand (P^P). The former exhibits three different sizes, with the ring made of 30, 37, and 42 atoms (see Figure).



[Cu(m30)(POP)]BF_4 [Cu(m37)(POP)]BF_4 [Cu(m42)(POP)]BF_4

At ambient temperature, the three complexes exhibit thermally activated delayed fluorescence (TADF), which makes them good candidates for singlet harvesting in OLEDs.5 Interestingly, they are also characterized by the continuous motion of the ether moiety of the macrocycle across the P^P thread, a process that strongly depends on temperature and on the specific size of the macrocycle, as evidenced by ^{31}P-NMR. Below 200 K the motion of the macrocycle is prevented and this directly affects the electronic properties of the overall ensemble. Detailed temperature-dependent photophysical studies (emission spectra and excited state lifetimes) allows the determination of the singlet-triplet energy splitting of the three copper complexes.[5] Comparison of the three pseudorotaxanes with a simple reference system ($[Cu(dmp)(POP)]^+$) – dmp = 2,9-dimethyl-1,10-phenanthroline – evidences a substantial difference in the photophysical properties of the supramolecular species.

Parole chiave: luminescence,

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Ceramic Multilayer for Energy Applicantions

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Layered ceramic composites, due to the possibility of combining layers of different composition and/or microstructures, have been widely exploited for energy applications.
Even if these structures are generally produced through well established and industrialized technologies, their fabrication generally requires specific expedients to avoid detrimental defects such as cracks, delamination, warping, unsuitable microstructure/densification, cross-contamination, phases deterioration, etc. In this work, the key-issues related to the ceramic multilayers production were investigated, analysing, as case-study, Solid Oxide Fuel Cells and Electrolyzers (SOFC and SOEC), Na-β-alumina batteries and dual phase ceramic membranes for hydrogen permeation. These devices were successfully produced by tape casting/screen printing by carefully controlling each step of the productive process.

Keywords: Ceramic Multilayer, Tape Casting, Screen Printing

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Reduction of EnergyWaste Improving the Efficiency: the Case Study of Oled Degratation

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The quest for energy efficient devices, allowing in principle the broad use of renewable and green energy, is a *hot topic* in the current organic electronic technology researches. Likewise, the development and use of sustainable and (bio)degradable materials is a chemical-appealing and a long-term future challenge of optoelectronics.[1]
Organic light emitting diodes (OLEDs), among organic optoelectronic devices, are considered the new reference technology suited for display and lighting applications. This is due, above all, to the OLEDs intrinsic low driving potentials (2-5V) and the broad color tunability.
Yet, one of the main issues in OLED technology is the stability of the emissive organic materials. OLED degradation occurs because of the accumulation of non-radiative recombination centers and luminescence quenchers at morphological and chemical defects and results in *increased power consumption*. In this contest, the study of degradation pathways, ultimately leading to OLED failure, is essential to meet the device lifetime and efficiency requirements.[2]
Herein we report our studies and understandings on the degradation mechanism in the model blue emissive OLED based on the "Firpic" complex (Figure 1). We coupled photophysical and thermal studies, device fabrication and chemical/analytical tests with thorough theoretical investigations in order to understand the degradation mechanisms acting on the working devices and thus define the boundary conditions for their suppression.[3]
In the talk it will be also presented an overview of the ongoing activities of the group in the fields of Near-Infrared[4] emission and the *light-to-energy conversion* researches.[5]
Our activities are organized in a feedback scheme between material design and synthesis, device development and stability investigations; the work is supported with the infrastructures of the SmartMatLab Center.

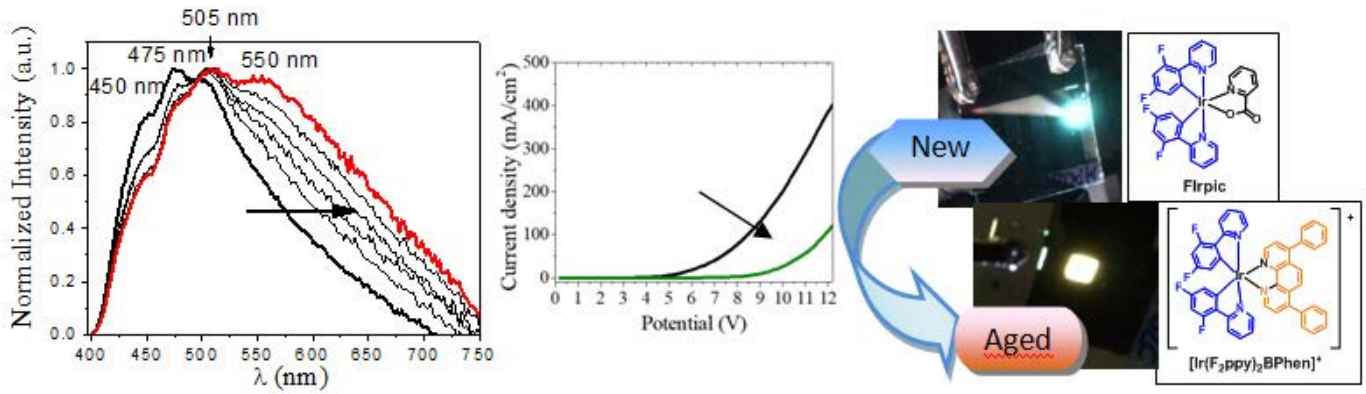

Figure 1. "Aging" effects on the optical and electrical features of the OLED: *left,* electroluminescence spectral evolution; *middle,* I/V profile showing current drop and potential raise; *right,* perceivable color alteration. Chemical structure of *Firpic* and the entrapped degradation product.

Parole chiave: energy efficiency, light emission, light harvesting, OLED technology, degradation pathways

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The Dark Side of the Moon: Organic Molecules for Perovskite Solar Cells

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Extensive research efforts are currently directed towards to the development of low-cost photovoltaic technologies, among which perovskite solar cells (PSCs) hold much promise. Indeed, due their wide range light absorption and charge mobility properties, three-dimensional (3D) hybrid perovskites of the formula AMX_3 (e.g. A = CH_3NH_3+ or $HC(NH_2)_2$+; M = Pb^{2+} or Sn^{2+}; X = Cl^-, Br^- or I^-) are appealing materials for many optoelectronic applications including light to electricity conversion. The unparalleled fast growth of photovoltaic performance observed with this technology has been boosted by the development of tailored organic hole transporting materials (HTM). We recently developed a convenient, broad scope synthesis of molecular HTM based on spiro configurated scaffolds containing dithiophene units, by which a wide library of HOMO-LUMO tuned HTMs was made available [1]. The electrochemical, photophysical and charge transport characteristics of these compounds are currently investigated in depth in collaboration with the team of Prof. M. K. Nazeeruddin (EPFL, Switzerland) [2], and tested in PSCs. One of these HTM, featuring an unprecedented fluorene–cyclopentadithiophene core, led to PCE of 20.2%.[3] Molecularly engineered molecules from our library proved to be particularly suited for mesoscopic $[HC(NH_2)_2]PbBr_3$ PSC [4]. Encouraged by these results, we turned our attention to another class of potential HTM, namely metallo-phthalocyanines. Preliminary tests revealed that the functional performance of these highly chemical and thermally stable compounds can be enhanced by molecular design [5].

Parole chiave: Organic synthesis, Hybrid perovskite, Solar cells, Charge transport

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CO_2 Separation by Advanced Membrane Operations

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Membrane-based gas separation systems are today widely accepted as green processes and, in many cases, used as a unit operation for generation, separation and purification of gases in chemical, petroleum, gas and energy industries. There are several applications of membrane gas separation as well membrane materials and membrane modules solutions available in chemistry and energy sectors. CO_2 separation from flue gas coming out from a power plant or a cement industry, as well as CO_2 from biogas and natural gas are examples of these fields. Polymeric membranes, thermally rearranged polymer membranes, mixed matrix membranes, etc. are examples of membranes investigated c/o the ITM-CNR for separating gases, such as, CO_2, CH_4, etc. of interest for many industrial cycles.
Membrane engineering, together with material science, covers a fundamental role in the development of this technology and its scale-up. Mass transport properties (e.g., flux and selectivity) of these membranes were analyzed feeding gas mixtures, with different content of water vapor and other aggressive components, these being one of the crucial assets for moving towards to real applications [1-3]. We also analyzed the mutual effect of the species present in the mixtures, responsible of the membrane selectivity variation, for CO_2 and CH_4 mixtures with N_2, H_2, CO, etc. Membrane aging owing to water vapor, physical compaction, thermal cycles and contaminants were and are currently under investigation as well with long term (hundred days) characterizations [4]. Modelling assists experimental analysis for a unified approach in advanced membrane unit operations. We developed a tool for analyzing membrane-integrated systems identifying suitable operating conditions and proposing possible process solution for achieving the desired separation [5, 6]. Among the main results achieved, we identified and successful applied a procedure for restoring membrane permeance and selectivity, after long-time operations.

Parole chiave: CO_2 capture, CH_4 purification, gas separation and treatment, long-time separation, restoring membrane permeance and selectivity

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Targeting Aβ for the Diagnosis and Therapy of Alzheimer's Disease

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The aggregation of peptide/proteins is often related to a number of pathological conditions. For example, the oligomerization and fibril formation of the Amyloid-beta peptide (Aβ), contributes to the development of Alzheimer's diseases (AD). The inhibition of the pathogenic aggregation of Aβ peptides might be a therapeutic strategy for curing AD.
Several approaches have been used to inhibit the aggregation of soluble Aβ monomers, either by stabilizing native conformations or by preventing β-strand intermolecular interactions between Aβ monomers. Molecular insights into the structure and composition of early oligomeric aggregates of Aβ, are essential for understanding the aggregation process and, ultimately, the cause of the disease. Despite the fact that the oligomeric form is a very important intermediate species, information on the structural and compositional properties is very limited, due to the extremely low concentrations and transient nature of these oligomers. We synthesized a series of water soluble small bio-conjugated compounds, in which the peptide moiety recalls the hydrophobic sequence of Aβ. This novel class of inhibitors were demonstrated to affect the kinetic of aggregation of the amyloid peptide at the very early stage, i.e. when Aβ's oligomer forms start to assemble. This suggests the presence of an underlying mechanism of molecular recognition involving these peptide based inhibitors and the amyloid peptide. Our aim is to shed light into a working mechanism in order to get useful information for the further studies of analogous derivatives as novel theranostic agents.

Parole chiave: Amyloids, peptides, bio-conjugation, theranostic, biomarkers.

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Polypharmacology-Based Strategies in Alzheimer's Disease: the Yin and the Yang of Acetylcholinesterase Inhibition

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Drug discovery and development is a complex and expensive process. Due to the exponential growth of molecular data and fast advancement in technologies, the efforts of drug discovery have been tremendously amplified. The philosophy of drug design has been transformed from "one drug - one target" to "one drug - multiple targets", coined as polypharmacology [1]. Polypharmacology is emerging as the next paradigm of drug discovery. Polypharmacological phenomena includes: (i) single drug acting on multiple targets of a unique disease pathway, or (ii) single drug acting on multiple targets pertaining to multiple disease pathways. In addition, polypharmacology for complex diseases, like Alzheimer's disease, is likely to employ multiple drugs acting on distinct targets, that are part of a networks regulating various physiological responses.
The approach needs the systematic integration of the data derived from different disciplines including computational modeling, X-ray crystallography, synthetic chemistry, *in vitro / in vivo* pharmacological testing, and clinical studies.
We report on the structure-activity relationships of novel multi-target direct ligands for the potential treatment of Alzheimer's disease, designed by combining tacrine / galantamine fragments to distinct pharmacophores *i.e.* juglone, memantine, benzofuran, nicotine and melatonin, with a linker of a suitable length. The compounds displayed excellent acetylcholinesterase inhibitory potencies and interesting capabilities to block amyloid-β aggregation and / or to bind the N-Methyl-D-Aspartate Receptor [2,3,4].

Keywords: Alzheimer's disease; Structural and mechanistic enzymology; Structure based drug discovery

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Classificazione di Oli Extravergini d'Oliva della Sardegna Attraverso l'Uso della Metabolomica ^{1}H-NMR

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La qualità e le proprietà fisico-chimiche dell'olio extravergine di oliva (EVOO) sono influenzate da fattori genetici, tecnologici, agronomici e ambientali [1]. Gli EVOO coltivati a diverse altitudini presentano significative differenze nelle percentuali relative di acidi grassi [2]. In letteratura è riportato che la temperatura e l'umidità della zona di crescita influenzano la composizione dei grassi degli EVOO, la concentrazione di esteri diacilglicerolici [3], di squalene e steroli, nonché il profilo dei volatili [4, 5].
In questo studio, EVOO della cultivar Bosana di Sardegna (Italia) sono stati studiati attraverso un approccio metabolomico basato sull'NMR, con l'obiettivo di evidenziare le influenze dell'ambiente di coltivazione sulla composizione degli oli.
La ricerca si basa su una rete sperimentale rappresentata da oliveti tradizionali monovarietali di Bosana e suoi sinonimi (Palma, Sassarese e Tondo Sassarese), condotti in coltura asciutta e con piante di età superiore ai cinquant'anni, ricadenti su quattro tipologie geo-pedologiche: calcari, basalti, graniti e alluvioni.
Gli spettri ottenuti da analisi NMR (Spettrometro Bruker Avance II 600) sono stati digitalizzati (bucket width 0.04 ppm) e sottoposti ad analisi statistica col software SIMCA-P 13.0 (Unimetrics); i dati sono stati scalati in maniera univariata, e sono state effettuate analisi O-PLS-DA.
La classificazione tramite analisi discriminante evidenzia che le differenti tipologie di suolo influenzano la composizione degli oli soprattutto nella componente polifenolica. L'esperienza conferma la validità del metodo NMR quale importante strumento per la caratterizzazione dell'influenza ambientale nella composizione dell'olio vergine di oliva.

Parole chiave: EVOO, Composzione, Origine Geografica, DOP, Food Security, OPLS-DA

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Potent Non-Covalent Inhibitors of Caspase-1 Targeting Neuroinflammation in Neurodegenerative Diseases

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Recent studies have shown the pivotal role of innate immune activation in the pathogenesis of major neurodegenerative diseases. It has been discovered that microglia and other cell of the brain innate immune system, may be activated by misfolded proteins or aberrant endogenous molecular patterns that are accumulated in the brain of patients affected by several neurodegenerative disorders. These stimuli are responsible for chronic neuroinflammation by triggering the inflammasome's formation and subsequent caspase-1 activation. Proinflammatory cytokines are processed by active caspase-1 into their mature form leading to cytokines production and, ultimately, chronic inflammation. Furthermore, the extensive generation of proinflammatory cytokines (IL-1β, IL-18) mediated from activated caspase-1, leads to pyroptosis that plays an important role in several neurological diseases. Moreover, recent findings indicate caspase-1 as a modulator for the activation of caspase-6 mediated axonal degeneration in AD. There is evidence that caspase-1 inhibition might effectively interfere with the onset and progression of neurological disorders. We have designed and synthesized new potent and selective non-peptidic, non-covalent, cell permeable caspase-1 inhibitors, which have shown a very high activity in suppressing the formation of IL-1β in LPS induced inflammation and to cross the BBB in PET experiments.

Parole chiave: Caspasi1 Inibitori, Neuroinfiammazione, Malattie Neurodegenerative.

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2-Hydroxy-8-methyl-1-oxaspiro[5.5]undec-3-en-5-one: a Natural-Product-Inspired Spiroketal with in vivo Efficacy in Mouse Model of Melanoma

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We have synthesised and identified 2-Hydroxy-8-methyl-1-oxaspiro[5.5]undec-3-en-5-one (1) as a new promising antitumor agent with *in vivo* activity on a murine melanoma model. Compound 1 showed potent dose-dependent antitumor efficacy in syngenic C57Black mice murine model of melanoma, suppressing the tumor growth by an average of 90% at a dose of 5 mg/kg by intra-peritoneum administration at alternate days for 15 days. It also displayed high antitumor activity in the B16 cells in vitro with nanomolar EC50 value. In addition to the proapoptotic and telomerase inhibition activity, compound **1** has shown to inhibit cell migration and to strongly reduce the HIF1α expression, that is considered a regulator of multiple cellular functions related to the progression from primary to metastatic cancer disease. Therefore, although the full mechanism/s of action of this molecule has yet to be completely elucidated, spiroketal **1** is a promising antitumor drug candidate for the clinical treatment of melanoma and various cancers.

Parole chiave: Spiroketal, anticancer, proapoptotic, telomerase inhibitor.

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Extremophiles for Astrobiology Studies

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Astrobiology studies the origin and evolution of life on Earth and in the Universe. According to the panspermia theory (Zagorski, 2007), life on Earth could have emerged after transfer of extraterrestrial life forms (most probably microorganisms) transported by radiation pressure or by meteorites on the Earth's surface. The transfer from one planet to another requires the ability to survive to several extreme environmental parameters (absence of oxygen, of water and of gravity; exposition to ionizing radiations; extreme temperature's variations, etc). Therefore, the study of extremophiles, i.e. bacterial species able to live in conditions incompatible with life from an anthropocentric point of view, can be relevant to Astrobiology studies: their ability to live in extreme conditions suggests that most probably extremophiles have been among the first living organisms that colonized the Earth. For these reasons they are the object of attention for astrobiology researches (Moissl-Eichinger et al., 2016).
Here, we reported the ability of the thermophilic species *Geobacillus thermantarcticus* (a bacterium isolated from Mount Melbourne, an active volcano in Antarctica) to survive after exposition to simulated spatial conditions (temperature's variation, desiccation, X-rays and UVC irradiation). The response to the exposition to the space conditions was assessed at a molecular level by studying the changes in the morphology, the lipid and protein patterns, the nucleic acids. *G. thermantarcticus* survived to the exposition to all the stressing conditions tested, since it was able to restart cellular growth in comparable levels to control experiments carried out in the optimal growth conditions. These results suggested that *G. thermantarcticus* could be a good biological model for astrobiology studies since it was able to repair the possible modifications induced by stressing space conditions thus counteracting the harmful effects of exposition to space conditions (Mastascusa et al., 2014; Di Donato et al., 2017).

Parole chiave: astrobiology; extremophiles, simulated space conditions

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StOrMoDB/ELN: a New, Versatile Integrated Chemoinformatic Platform

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StOrMoDB/ELN (Structurally Oriented Molecular Data Base/Electronic Laboratory Notebook, the word "Stormo" in Italian means "flock of birds", https://stormodb.na.icb.cnr.it) is a molecular database/electronic lab notebook completely developed in-house at ICB-CNR, only employing Open Source chemical libraries and development/deployment tools. Among its numerous features, the management of organometallic compounds deserves a special mention, since, to the best of our knowledge, this is the first (at least among publicly available) data base capable of managing the topological info about "pseudocenters" and "metal coordination bonds" required to describe bonding in this class of molecules.
Some of the most relevant field sections of the data base are: Origin (with differential sets of fields for natural vs. synthetic molecules), Targets/Applications, Atoms, Bonds, Functional Groups (automatically identified during structure input), Spectra and Assays.
Presently, users with a valid ICB-CNR mail account are allowed to create and edit molecules and notebooks, while other users can search the database and use the standalone tools for drawing molecules, calculating some properties and viewing spectra and chromatograms saved locally in JCAMP-DX format.
Molecules can be introduced by drawing the structures with the online tool, by loading single structure files in different formats, or multiple structures with a descriptive file containing mandatory information for each entry. In all cases, input molecules will be carefully checked before creating the new entry(ies). Also queries can be performed with different methods and criteria, e.g. name (full/partial), mol weight and/or keywords, formula, SMARTS patterns, multiple functional groups (combined with boolean operations), or drawing a molecule/fragment and searching by either similarity or by substructure.
An interesting application of the data base (especially for dissemination and teaching purposes), of which two examples (on spices and natural dyes) are shown in the "Exhibit" menu of the homepage, is the development of user-friendly interfaces dedicated to classes of products/goods/living species, providing different types of information on each item, ending with a DB query retriving all the relevant compounds associated to the selected item.
In its final form, StOrMoDB will represent a highly-integrated chemo/bioinformatic platform, including a data base, a lab e-notebook and supporting tools for molecular modelling. This platform will provide researchers involved in biomedical and pharmaceutical projects (but also in ecological, cultural heritage, agrifood,… projects) with tools specifically targeted at easing and supporting development of diagnostic or pharmaceutical applications from natural products. The data base integrates different kinds of experimental data (chemical, chemico-physical, spectroscopic, synthetic pathways, use and occurrence in nature, biomedical and pharmacological properties), with computed/predicted properties (chemico-physical properties, molecular descriptors).
In addition to this talk, live sessions will be possibly held during the meeting.

Parole chiave: Chemoinformatics, Molecular Database, Electronic Lab Notebook

Live Demo of StOrMoDB/ELN: a New, Versatile Integrated Chemoinformatic Platform

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Live demos and training sessions for StOrMoDB/ELN (Structurally Oriented Molecular Data Base/Electronic Laboratory Notebook, https://stormodb.na.icb.cnr.it) will be held by the authors, showing and explaining the main features of both DB and ELN. Also the standalone tools and the user-friendly interfaces available at StOrMoDB/ELN mainpage will be demonstrated.
This demo is complementary to the oral presentation of Dr Amodeo introducing StOrMoDB/ELN.

Parole chiave: Chemoinformatics, Molecular Database, Electronic Lab Notebook

Exploitation of Marine Genetic Resources: Walking on the Border of Basic Science

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Biotechnology involves studies of molecules, cells and organisms with the aim of understanding how biological processes work, and harnesses cellular and biomolecular processes to develop technologies and products that help improve our lives and the health of our planet. We often think of biotechnology as a new area for exploration, but mankind have used the biological processes for thousands of years since the domestication of crops and livestock made civilizations to prosper. Nowadays, access to new genetic resources and advanced technologies make it possible to study biological reactions and systems better than just a few years ago. Modern biotechnology provides breakthrough knowledge to combat debilitating and rare diseases, reduce our environmental footprint, feed the hungry, use less and cleaner energy, and have safer, cleaner and more efficient industrial manufacturing processes. In the last years we have intensified our efforts on the exploitation of marine organisms for new applications in human wellbeing, energy and food. As part of a public institution, our investigations fall in the very early phase of the development of products and processes but increasingly they meet the requests of industrial endusers. Here we present a brief overview of our research platform and approach [1] on cultivable unicellular organisms with specific examples on how the understanding of chemistry and biochemistry of natural functions can create novel solutions for biotech applications.

Parole chiave: blue biotechnology, bioproducts drug discovery

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Profiling Cancers Toward a Real Precision Medicine

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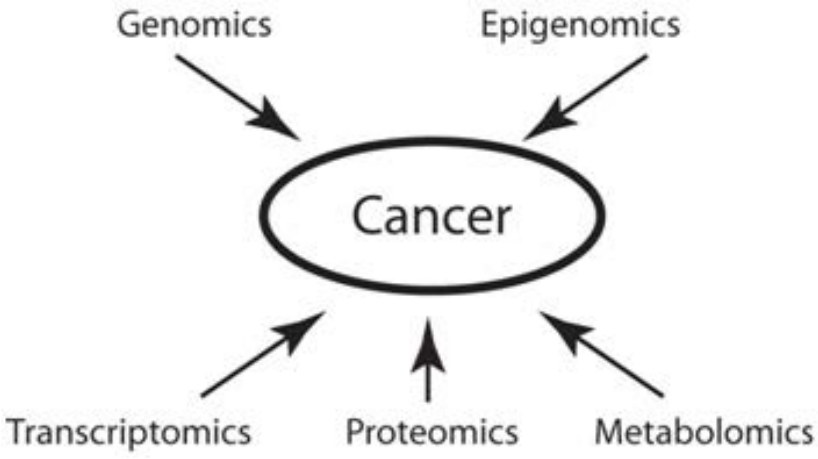
Cancer causes significant morbidity and mortality worldwide, and is the area most targeted in precision medicine. Precision medicine is an approach that takes into account individual differences to guide disease prevention and treatment and oncology is the most prominent field targeted for precision medicine. Recent development of high-throughput methods enables detailed "omics" analysis of the molecular mechanisms underpinning tumor biology, which represent the starting point "to deliver the right treatment at the right time, every time, to the right person". Next-generation sequencing (NGS) technologies are the approaches which are being mostly transferred to the clinical practice, allowing for the characterization of the cancer genome associated with treatment decisions, offering the opportunity to increase the therapeutic efficacy by targeting oncogenic driver alterations. However, it is difficult to integrate genomic profiling with the decision-making process of cancer treatment, as the interpretation of genomic data is still challenging. To date, no sufficient guidelines for implementing NGS test in cancer clinical practice are well established worldwide.
Our group is strongly involved in assessing validation best practice guidelines for NGS gene panel testing



of pathogenetic gene variants in some types of cancers - mostly, malignant melanoma and lung carcinoma. Development of specific target panels represent a relevant, highly scalable, and robust tool that is easy to implement and can be fully adapted to daily clinical practice in determining cancer actionable gene mutations. Moreover, subsets of cancer patients who result as "orphan" of actionable molecular alterations or, alternatively, present intrinsic/acquired resistance to existent antitumor treatments may represent the elective target group for testing new drugs.

Parole chiave: Precision medicine - Molecular cancer classification - Targeted therapy

Ringraziamenti:
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Interfacial Properties of Ophthalmological High-Viscosity Silicone Oils in the Presence of Blood Proteins.

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We report a study of the effects of different blood serum proteins on the physicochemical properties of the silicone oils/aqueous phase interface. High-viscosity (larger than 1000 cs) silicone oils (SO) are extensively used in ophthalmologic surgery to treat a variety of pathological or traumatic vitreoretinal conditions, as substitutes of the vitreous humour: the gel-like substance filling the cavity in the eye bulb. In spite being one of the most utilised vitreous substitute, SO invariably emulsifies with the aqueous phase produced in the eye. This may result in a number of post-surgical complications from moderate to serious.
The blood proteins produced by inflammatory processes have been identified as an important co-factors responsible for the emulsification. Understand how the adsorption of these proteins affects the physicochemical properties of the interface and how these properties are related to the SO emulsification is a mandatory step to conceive and implement new strategies to hinder the emulsification of SO for vitrectomy.
We have therefore investigated the dynamic interfacial tension and the dilational rheology of the SO-aqueous phase interface in the presence of key serum proteins within the physiological concentration range. The measurements have been performed in the proper characteristic time windows by using a Drop Shape tensiometer. The results show that the adsorption of proteins at the liquid interface reduces the interfacial tension to values compatible with an increased tendency to emulsify and provides values of the dilational viscoelasticities compatible with a good stability of the resulting emulsions.

Parole chiave: liquid-liquid interface, silicone oil, blood proteins, vitreous substitute

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Osteointegrative Functionalization of Dental Implants: a New Synergic Approach

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Titanium and its alloys have been widely used for dental implants due to their excellent combination of strength-to-weight ratio, excellent corrosion resistance and biocompatibility [1]. In order to improve osseointegration, the titanium surface is generally functionalised. A typical methodology of surface modification, able to efficiently change the surface chemistry of a metallic implant, is the coating of the titanium substrates with layers of bioactive calcium phosphate ceramics (CPCs) [2]. Moreover, titanium implants are usually processed in order to increase the surface roughness in a controlled way: sandblasting and/or chemical etching are approaches commonly used.
With the aim of improving the adhesion strength between the Ti substrate and the CPC layer, the insertion of dense and compact ceramic interlayers is reported to be useful [1]. Indeed, they improve the film to implant adhesion both reducing the thermal mismatch between the metal and the calcium layer and increasing the amount of -OH sites available. Among various ceramics, crystalline titania (TiO_2) has been extensively used as an inter-layer thanks to its well-known biocompatibility and bioactivity [1].
In this work, three types of Ti substrates (machined, sandblasted, and sandblasted/acid etched) were initially coated with a crystalline, dense and compact TiO_2 inter-layer via MOCVD. Then, a discontinuous and homogenously spread CPC top-layer was obtained by means of spray pyrolysis technique. Finally, a thermal treatment at high temperature was carried out in order to crystallize the final composite material. Preliminary investigation on the influence of the pristine substrate morphology on TiO_2 crystalline structure, morphology, surface wettability and *in vitro* acellular bioactivity is here presented. Moreover, the CPC/TiO_2 composite material was also characterized by means XRD, SEM and release tests.

Keywords: osteointegration, CPC, TiO_2, bioactivity, dental implants.

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Design and Development of Nano-Carriers for the Targeted Release of Antimicrobial and Antitumoral Molecules

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Among the major properties that should characterize a modern drug, the ability to overcome a range of physiological barriers and the specificity for a therapeutic target are probably the most important. To this aim, it is often necessary to find a carrying vector able to enhance drug delivery and specificity to improve its therapeutic efficacy. The main targets of our projects are to find new molecules to fight the threatening problem of microbial resistance and developing efficient and specific anticancer drugs. To this aim we are developing in collaboration with other Universities and Research entities various types of nano-carriers based on the combination of biocompatible nanoparticles (NPs) and peptides bearing bioactive specific sequences. The production of NPs is based onto two types of scaffolds a) the self-assembly viral protein VP6 obtained by cloning the corresponding gene from human Rotavirus A and b) chitosan polymers. These NPs once loaded with bioactive molecules (natural products, drugs, iRNAs etc) are hence “decorated” with appropriate peptide sequences which, depending on the desired purpose, may acquire biological features such as cell penetrating properties to enhance the delivery of the drugs within cells, or recognizing surface cell receptors in order to specifically target their payload.
We are also developing chimera peptides linked to biologically active natural products, composed of different sequences, each with a specific function to target cancer cells by their overexpressed receptors.

Parole chiave: drug delivery, nanoparticles, bioactive peptides

NMR Spectroscopy: a Valid Tool in Targeting Bioactive Molecules

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NMR spectroscopy is a well establish analytical method in structural characterization of macromolecules. In these last years, NMR has been accepted as a preferential analytical method for mixture investigations, playing an important role in the "omics" technologies. Food matrices, as well as plant extracts and by-products, have been investigated, not only in metabolite fingerprinting approaches but also in sourcing for bioactive compounds[1-5]. The NMR approach takes the advantage of analyzing the metabolite content with a single experiment in a non-destructive way. Moreover, very simple or none sample preparation is required, thus making this technique very low demanding in terms of data acquisition and sample preparation. In plants, several studies are present concerning the metabolic investigations by NMR followed by the multivariate statistical analysis of data, allowing easier data interpretation, marker and/or new molecules discovery. Comparison of metabolite profile of treated or non-treated samples is also facilitated. In the present communication, the potentiality of the NMR approach will be presented with the aid of different practical examples.

Parole chiave: NMR, metabolomics, bioactive compounds, nutraceuticals

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Isolation, Digital Detection and Characterization of Biological Nanoparticles for Exosome-Based Diagnostics

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Cells produce and release membrane vesicles in cell cultures and different bodily fluids. A particular type of such vesicles, named exosomes, are 30-100 nm in diameter, their lipid composition depend on the cell of origin and their surface is decorated with integrins, transmembrane proteins, and glycoproteins; they contain genetic material and proteins. Exosomes are known to mediate communication between cells, playing an essential role in inflammation, cellular homeostasis, survival, transport and regeneration; accordingly, minimally-invasive diagnosis of a number of diseases can be achieved through detection of these vesicles. In particular, exosomes are considered valuable for liquid biopsies in cancer diagnosis since they carry molecular and proteomic cargo from their tumour cell of origin. In human cerebrospinal fluid (hCSF), exosomes are rich reservoirs of biomarkers for neurological disorders and there is increasing evidence that deregulation of vesicle secretion play a pathological role in Alzheimer's disease. Despite they hold the great promise of revolutionizing the standard of clinical care, their detection and molecular profiling is still technically challenging due to their small dimension and low refractive index. In this work we present a method based on Single Particle Interferometric Reflectance Imaging Sensor (SP-IRIS) that allows multiplexed phenotyping and digital counting of various populations of individual exosomes (>50 nm) captured on a protein microarray-based solid phase chip. We demonstrate these concepts using purified exosomes from cell culture and directly from hCSF. Our interferometric imaging method could capture, from a very small hCSF volume (20 uL), nanoparticles that have a size compatible with exosomes, using antibodies directed against tetraspanins. With this unprecedented capability, we foresee revolutionary implications in the clinical field with improvements in diagnosis and stratification of patients affected by different disorders.

Parole chiave: exosomes, interferometry, microarrays, diagnostics

Riferimenti:

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Successful Applications of Computational Modelling to Different Stages of the Drug Discovery Process

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In the absence of experimental structures, computational methods are used to study protein mechanism, to assess the biological role of mutations and their effect on protein function, to identify hits by virtual screening (1). At ICRM-Rome high performance computational resources, equipped with a variety of research software packages, are available for modelling three-dimensional target structures and identifying small molecules of therapeutic interests by molecular docking. It is widely accepted that docking to homology models is more challenging than docking to crystallographic structures of proteins. This presentation will show how if the three-dimensional structure of the biological target is not available, protein models represent an alternative for ligand docking and characterization of protein structural properties. Specifically the results obtained for biological targets in autoimmune diseases, also rare autoimmune diseases, and solid tumours will be highlighted where we used a combination of homology modelling and virtual screening methods to find novel lead structures (2). Protein modelling applications to characterize dystroglycanopathy-related proteins (3) and identify druggable pockets in antibacterial targets (4) will be also outlined.

Parole chiave: Protein modelling; molecular docking; Computer-Aided-Drug-Design

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A Data-Matrix Method for Multiparameter Monitoring of Cell Cultures

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Cell culture is one of the most used tool in a large variety of life-science studies, ranging from single cell investigation to diagnosis and treatment. Monitoring the cells adhered on a substrate, their morphology, spatial distribution and the ability to migrate gives access to quantitative assessments of cell wellness, differentiation stage and fate. Here, we address these issues by introducing the data-matrix technology in cell biology as an efficient method for easy and fast multi-parameter monitoring of cell cultures, exploiting the know-how developed for error handling in digital information technology. The approach is based on the measure of reading errors induced by intervening cells upon checking a fluorescent data-matrix code placed behind them by a smart-phone. The process has been demonstrated with several immunostained model cell cultures, delivering, in real-time, the evolution of the number of cells, coverage and related information, such as mean area and viability moreover the method has been proven to measure the transfection efficiency in human embryonic kidney. This work opens the way to the application of robust knowledge developed for digital technology in life science, opening an enormous quantity of possibilities.

Parole chiave: Cell culture, data-matrix technology.

Ringraziamenti: The activity has been supported by national Project N-CHEM, Flagship NANOMAX.

Identificazione ed Ottimizzazione di Nuovi Scaffolds Molecolari di Interesse Oncologico

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Lo sviluppo di molecole innovative per la cura di patologie oncologiche continua ad essere un terreno particolarmente battuto nella ricerca di nuove strategie terapeutiche. Proiezioni statistiche, per i prossimi decenni, non sono confortanti, le patologie tumorali assumeranno valori sempre più crescenti. Nonostante siano stati compiuti molti passi avanti, ancora molto resta da fare. La comprensione dei meccanismi molecolari degli eventi cellulari legati al mancato controllo della proliferazione cellulare rimane ancora un obbiettivo da raggiungere. In tale contesto si inserisce la ricerca di seguito presentata volta alla progettazione, sintesi, ottimizzazione di substrati eterociclici opportunamente funzionalizzati. La multidisciplinarietà che caratterizza quest'attività, coinvolge aspetti di biologia molecolare, di tecniche computazionali (computer aided drug design), di metodologie biofisiche e di competenze di chimica organica (Fig 1). Pertanto, collaborazioni nazionali ed internazionali si rendono necessarie.

A seguito di screening antitumorale effettuato su 60 linee cellullari, inclusi tumori solidi e liquidi, i derivati

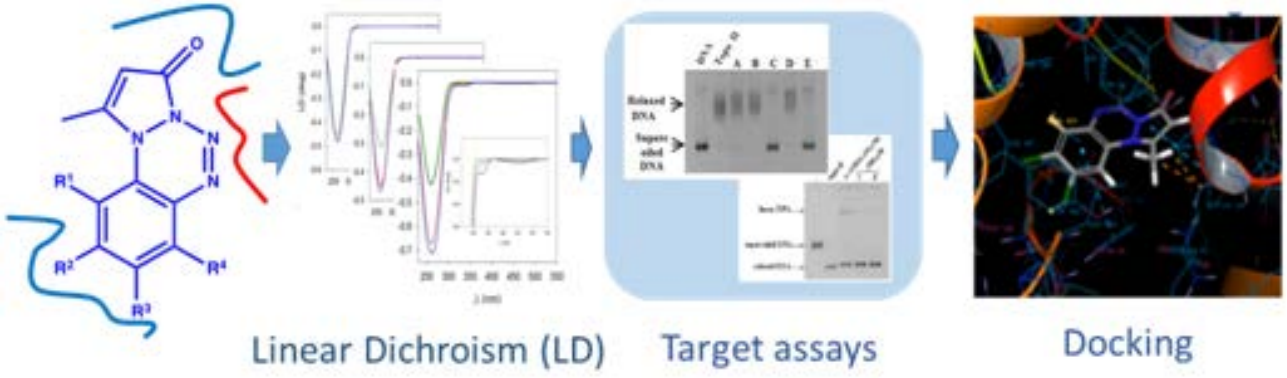

Fig 1. Indagini sul meccanismo di azione di derivati PBT dotati di potenziale attività antitumorale [a,b]

di sintesi PBT (small molecules) risultati attivi vengono sottomessi ad ulteriori approfondimenti volti alla comprensione del meccanismo/i di azione. L'analisi dei risultati, supportati da studi *in silico* getta le basi per la progettazione e la sintesi mirata di nuove entità molecolari più attive su biotarget specifici. Maggiori dettagli saranno forniti in sessione poster.

Parole chiave: Anticancer agents, DNA interactive, pyrazolo[1,2-a]benzo[1,2,3,4]tetrazin-3-one

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Ringraziamenti: NCI (National Cancer Institute, Bethesda MD, USA. Screening antitumorale su 60 linee cellulari, one dose/five doses in vitro test.

Bio-Inspired Synthetic Strategies of Hydroxyapatite Nanocrystals: from Biomineralization to Regenerative Medicine and Drug Delivery

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Understanding how living organisms form their extremely specialized mineralized structures, and identifying the organic molecules controlling the final crystal size, shape and polymorphism, which in turn determine their unique mechanical and biological properties, is highly relevant, not only on the fundamental knowledge side, but also as a source of inspiration for the design of advanced biomaterials. Hydroxyapatite (HA) nanocrystals are intriguing biominerals whose formation in the organisms is still far away to be completely understood. The HA biomineralization is a complicated process that arises on the interaction between ions, small organic molecules, collagen and non-collagenous proteins. The study of HA formation is crucial not only to understanding how living organisms form the mineralized structures of bones and teeth, but also to achieve synthetic advanced materials being a perfect replica of the biogenic material for application mainly in the fields of regenerative medicine and bone tissue engineering. In addition the increasing knowledge on the nucleation and growth of HA nanocrystals allows the design of advanced nanoparticles with high biological performances for drug delivery applications [1]. In this regard in our research group we have investigated two nature-inspired synthetic strategies to achieve a high degree of control over HA structure, properties and functions. In the first one HA nanocrystals were synthesized in presence of small dicarboxylic acids, i.e. citric, glutaric and hydroxycitric acid in order to understand how simple molecules and small variations in their molecular functional groups can affect growth and size of HA nanocrystals [2]. In the second one HA nanocrystals are growth upon amorphous substrates in presence of different amino acids forming highly oriented needles with a morphology very close to human enamel [3].

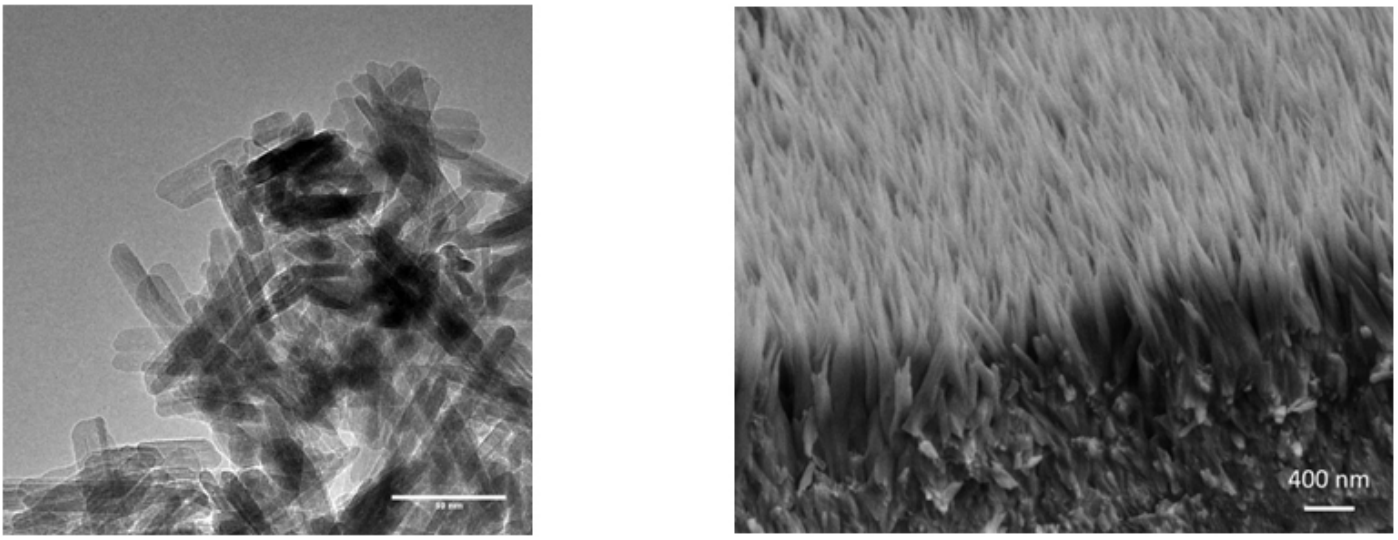

Figure 1. Left: TEM micrograph of HA nanocrystals synthesized in presence of citrate. Right: HA needles grew on calcium phosphate amorphous substrate.

Parole chiave: Hydroxyapatite, biomineralization, regenerative medicine, drug delivery

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Mineralizing Spider Network: A New Promising Hybrid Biomaterial

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Silk is the fibrous protein polymer spun into fibers by *lepidoptera* (spiders, silkworms, scorpions, insects); it is an attractive biomaterial for application in tissue engineering thanks to its biocompatibility, strength and elasticity. Silk is a complex hierarchical structures composed of repetitive protein sequences and it assembles in stacked hydrophobic *β-sheet* structures, highly crystalline, in a hydrophilic matrix. [1] The crystalline structures confers extraordinary mechanical properties while the aqueous domains are responsible for fiber elasticity and resiliency. Silk has exceptional mechanical properties, especially stiffness is comparable to the bone stiffness and it is 3-order of magnitude higher than the collagen while the high performances under compression are greater than the Kevlar. [2] For this reasons and to improve their performance in bone regeneration, the aim of this research is to nucleate hydroxyapatite (HA) into the spider silk by means of biomineralization process to develop a biomaterial with improved mechanical properties and an enhanced biomimicry and osteconductivity thanks to HA, the mineral phase of native tissues. The biomineralization refers to the natural processes by which organisms form minerals and consists in a complex cascade of phenomena by which natural organisms generates hybrid nano-structured materials hierarchically organized from the nano-scale to the macroscopic scale composed of an inorganic and organic components. Our research group paid a lot of attention to this process and started to develop materials with highly controllable and specialized properties inspiring by this process, hence HA nanoparticles was nucleated on polymeric matrix promoting the formation of a quasi-amorphous HA phase reproducing the chemical and physical features of the natural apatite. In the present study a mineral phase was nucleated on spider silk using different techniques such as neutralization, salt-mediated and SBF-mediated processes. The samples derived from three different spiders and the original draglines are composed of more smooth threads with a diameter of about 3 µm and aggregates of 9 µm diameter. The mineralization process was followed in time using time-laps equipment and the morphological evaluations highlighted that spider silk fibres were successfully coated with a homogeneous and thick crystalline calcium phosphate layer. Finally we can underline that the use of salts took to an uncontrollable crystals growth compared to the use of acid/base biomineralization reaction during which silk fibers act as template for the nucleation of the mineral phase which growth in form of nanocrystals in strictly contact with the fiber, similarly to what happen in nature during the ossification process.

Parole chiave: Spider Silk, biomineralization, reinforcement, tissue engineering

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Novel Multifunctional Ion-Doped Apatites with Enhanced Osteogenic and Antibacterial Properties

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A serious concern related to the implantation of biomedical devices is the occurrence of post-surgical infections [1]. Particularly, infections associated to bone implants frequently degenerate into osteomyelitis, a severe clinical problem, very difficult to be completely eradicated [2, 3]. In this respect the development of new materials integrating the ability to promote and sustain bone regeneration with prolonged and effective protection against bacteria is a topic of great relevance in bone surgery. Hydroxyapatite (HA) is the elective material for bone substitutes, and specific ion doping, particularly magnesium and carbonate ions, provide apatite with enhanced ability of inducing new bone formation. In this respect the present work describes the synthesis of novel multi-doped apatite phases with enhanced osteogenic and antibacterial ability, by neutralization method. The new materials were characterized by ICP and XRD analysis to evaluate the effect of the different doping on the apatite crystal features. Besides, in vitro analysis of human mesenchymal stem cells (hMSCs) behaviour, and of the activity of four different infective agents (*C. Albicans, E. Coli, P. Aeruginosa, and S. Aureus*) was carried out and correlated with the extent of ion release in the same medium, to elucidate the active mechanisms in bacterial inactivation. Rietveld analysis of XRD patterns demonstrated the effect of single and multiple doping on the cell parameters and crystal domains of the apatite lattice in the new materials. The single doping with Ga or Zn ions provided enhanced antibacterial activity, in respect to undoped HA whereas multiple doping including also Mg and CO_3 gave enhanced effect, associated with higher cell viability and ALP expression by MSCs.
The new multi-doped apatites are promising materials to develop bone implants and coatings simultaneously showing improved effect on new bone formation and prevention of bacterial infections.

Parole chiave: Biomimetic apatites, ionic substitutions, antibacterial effect, bone regeneration, magnesium, carbonate, gallium, zinc

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Effect of Membrane Properties on Neuronal Behaviour and Differentition

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In this study we report about the realization of different collagen-blend membranes by combining collagen with chitosan (CHT) or poly(lactic-co-glycolic acid) (PLGA) to enhance their properties and thus create new biofunctional materials with great potential use for neuronal tissue engineering and regeneration. Collagen blending strongly affected membrane properties in the following ways: (i) it improved the surface hydrophilicity of both pure CHT and PLGA membranes, (ii) it reduced the stiffness of CHT membranes, but (iii) it did not modify the good mechanical properties of PLGA membranes. The investigation of the effect of the different collagen concentrations on neuronal behavior once seeded on the novel membranes was also performed. Morphological observation demonstrated that the developed membranes, especially CHT/Col30, PLGA and PLGA/Col1, provided suitable microenvironments for neuronal growth owing to their enhanced properties. The most consistent neuronal differentiation was obtained in neurons cultured on PLGA-based membranes, where a well-developed neuronal network was achieved. Our findings suggest that tensile strength and elongation at break are key material parameters that have potential influence on both axonal elongation and neuronal structure and organization. Hence, our study has provided new insights regarding the effects of membrane mechanical properties on neuronal behavior, and thus it may help to design and improve novel instructive biomaterials for neuronal tissue engineering.

Parole chiave: Collagen-blend membranes • Neuronal cells • Neuronal differentiation

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Membrane-Based Approaches for the Biofabrication of Microtissues

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For the biofabrication of an organ or tissue is required a biomimetic approach that utilizes expandable cells, a cell-affinity biomaterial that serves as scaffold and an optimal bioreactor.
Micro- and nano-structured membrane bioartificial systems consisting of functional cells and polymeric membranes can be used for the creation of tissue analogous because of the high control at molecular level of cell microenvironment. These artificial systems compartmentalize cells in micro and nanostructured complexes providing a wide surface area for the cell adhesion and ensuring a continuous and selective transport of nutrients and metabolites to and from cells. Membrane systems are able to create a biomimetic environment governing the mass transfer of molecules that generate a precisely controlled microenvironment that mimic the specific features of in vivo environment. Attempt to engineering biological tissues in vitro have been pursued by applying novel concepts of bioreactor design and membranes to enhance the ability to trigger biological signals that promote the morphogenesis of tissue. This approach allowed the realization of microtissues inducing self-assembling process of spheroids through the use of membranes with selective permeability, specific surface and mechanical properties.
A designed approach has been utilized for the development of a 3D liver system. This approach makes use of primary human sinusoidal endothelial cells, stellate cells and hepatocytes that are seeded sequentially in a hollow fiber membrane bioreactors in order to mimic the layers of cells found in vivo. The organotypic system was maintained functionally active in the HF membrane bioreactor, which ensured a continuous perfusion of cells and the selective mass transfer of molecules to and from cell compartment creating a physiologically relevant microenvironment.
A novel membrane system was created to provide a 3D well-controlled microenvironment for neuronal outgrowth. Our recent investigations demonstrated the role of membrane properties as modulators of neuronal growth and network assembly and connectivity representing a first step towards the exciting and ultimate frontier of understanding the brain. Advanced membrane systems in flat and tubular configurations were able to guide the neurite outgrowth and orientation of neuronal cells. The high performing system built up in this study modulated and enhanced neuronal outgrowth, thanks to a synergistic action of the membrane properties and the uniform microenvironment of the device. The membrane system besides enhancing acquisition of neuronal phenotype guided the neurons into a defined aligned orientation according to the topographical cues offered by the membrane surface.

Key words: Membranes, microtissues, bioreactor, neuronal cells, liver cells

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Tacking on Protein Crystallization Challenge by Hybrid Materials

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Molecules in crystal form are required for several applications, such as purification, and academic studies, such as structural solution by X-ray diffraction. Regardless the application, getting the experimental conditions able to crystallize the specimen is not a trivial process, particularly if we want also optimize the crystallization process in terms of yield, starting material, speed, and diffraction quality of the crystal. Unfortunately, searching these conditions is trial-and-error time-consuming process, particularly in the case of protein molecules. A turning point in this field is represented by composite materials made of gel and membrane. These new materials was been conceived by ITM-CNR, and UNICAL (Arcavacata di Rende, Cosenza) and are able to enlarge the range of successful crystallizing conditions. For a long time, IC-CNR, ITM-CNR, and UNICAL are collaborating to develop and design these innovative materials. We have shown that these materials reduce protein concentration required for crystallization and make wider crystallization range of the protein molecule. Interestingly, resulting crystals have a better quality for diffraction experiment (signal-to-noise ratio and final crystallographic R-factor) than those produced by standard vapor diffusion.[1] Moreover, their features can be modified in a very controlled manner. For instance, we shown that the membrane patterning/roughness induced by including less than 1% of iron oxide nanoparticles provides a tool to promote and control heterogeneous nucleation without metal inclusion in the crystals. Due to the contact between gel portion and protein crystals, gel is able to penetrate in the crystals forming an inner structure made of gel.[2] So, crystal is protected from quick dissolution due to osmotic stress and becomes particularly suitable for industrial and biotechnological applications. We are exploiting the gel inclusion to develop materials made of membrane/gel able to immobilize and stabilize lysozyme crystals for food-preserving active packaging. Interestingly, lysozyme crystals obtained by these latter materials have higher anti-microbic than the protein in solution, possibly due to higher concentrated, pure, and active protein in the crystal than in solution. Moreover, we are developing materials able to purify antibody by crystallization directly from culture broth, with the aim to remove the expensive downstream purification processes that represent more than 60% of the final cost of the drug (AMECRYS Horizon2020-FET project). These composite materials represent an innovative concept that is proving adaptable to many applications. Properly combining gel portion and polymeric membrane, it is possible to reduce protein concentration required for crystallization with respect to the traditional techniques, control vapor diffusion by membrane, and protect and entrap crystals in the gel portion. In this way, protein crystals are suitable for soaking experiments because are protected from osmotic shocks and, moreover, their higher lifetime makes them exploitable in biotechnological application without the need of cross-linking or other chemical modifications.

Parole chiave: hybridmaterial, protein crystallization, protein crystallography, enzyme immobilization, protein purification

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Table Top X-ray Scanning Microscopy of Fiber-Like Materials

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A non-destructive structural and morphological characterization is required during the different fabrication phases of a novel material or for the investigation of a natural one. X-rays offer key features such as large penetration depth (up to several mm), short wavelength (Ångstrom) and atomic chemical contrast.
X-ray scattering-based scanning microscopy is today available in laboratory, as realized at the XMI-L@b1, thanks to novel synchrotron-like table-top microsources[1] which allow to reach high brilliance focused beams for ex-situ dedicated experiments. Examples will be given of table-top Small and Wide Angle X-Ray Scattering-based Scanning Microscopy of fiber-based materials investigated across different length scales[2]: atomic, nanoscopic as well as microscopic.[3,4,5].

Parole chiave: Imaging, Microscopy, X-rays, Fibers

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Analisi HPLC su Fase Stazionaria a Base Polisaccaridica: una Metodologia Innovativa ad Alta Sensibilità per l'Identificazione di Interazioni σ-hole Stereoselettive

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Il σ-*hole bond* è un'interazione non covalente tra un atomo covalentemente legato (donatore), che porta una regione caratterizzata da un potenziale elettrostatico positivo (σ-*hole*) su orbitali non popolati σ*, e un sito nucleofilo (accettore). L'identificazione e lo studio di queste interazioni in soluzione è piuttosto complesso rispetto a quanto accade allo stato solido. Infatti, in soluzione, le interazioni possono essere influenzate dalla libertà conformazionale delle molecole, dal disordine generato dal mezzo solvente e da effetto-solvente sia sul donatore che sull'accettore. In genere, sistemi perfluorurati e *N*-eterocicli cationici sono in grado di attivare potenziali σ-*holes* e generare forti donatori, identificabili attraverso tecniche spettroscopiche, in particolare NMR.[1] D'altra parte, donatori neutri iodurati e bromurati sono richiesti per applicazioni *real-life*, in particolare, nel *drug discovery* e in chimica supramolecolare. In questo caso, le tecniche spettroscopiche risultano poco sensibili per l'identificazione di interazioni deboli generate da donatori poco attivati.
Recentemente, impiegando una serie di 4,4'-bipiridine alogenate,[2-4] con capacità σ-*hole*-donatrice variabile, e due polimeri a base polisaccaridica come accettori, con diversa forza come basi di Lewis, è stato messo a punto un protocollo basato su uno screening ortogonale con tecnologia HPLC allo scopo di identificare e studiare σ-*hole bonds* deboli in ambiente chirale solvatato. La metodologia è stata sviluppata tenendo conto che la forza di interazioni tipo σ-*hole bond* dipende proprio da tre fattori, ovvero la profondità del σ-*hole* sul donatore (analiti bipiridinici), la basicità di Lewis dell'accettore (polimeri polisaccaridici) e il mezzo solvente (fase mobile). Il protocollo proposto ha permesso di studiare l'andamento dell'interazione al variare della polarità del mezzo solvente. Il metodo può essere esteso anche a fasi mobili contenenti acqua. A questo proposito, è importante ricordare che per applicazioni in chimica medicinale l'acqua è il solvente esclusivo e il comportamento di σ-*hole bonds* in acqua è ancora poco compreso e richiede ulteriori studi.

Parole chiave: Chiralità, HPLC, Potenziale elettrostatico, Riconoscimento molecolare, σ-hole

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Functionalization of Exfoliated Black Phosphorus with Metal Nanoparticles and Application of the Nanohybrid in Catalysis

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Black phosphorus (BP) has a layered structure analogue to graphite and recently[1] it was discovered that can be exfoliated down to the monolayer. In this way, a new member of the growing family of 2D materials, named *phosphorene*, the all P-counterpart of graphene, was successfully isolated. Single and few-layer BP (2D BP) have been obtained by several techniques,1 in our labs good quality phosphorene flakes were prepared by sonicating BP microcrystals in dimethylsulfoxide (DMSO).[2] Currently, we are exploring its functionalization with transition metal nanoparticles,[3] addressing in particular the study with nickel. Morphological analysis carried out by TEM showed nickel nanoparticles are well dispersed on the surface of 2D BP (see figure) and interestingly the nanohydrid Ni/2D BP has an improved stability in ambient conditions in comparison to pristine 2D BP. This feature prompted us to use Ni/2D BP as catalyst in the semihydrogenation of phenylacetilene and afforded good catalytic activity and high selectivity to styrene preserved after recycling tests.

Keywords: black phosphorus, nickel, nanoparticles, 2D materials.

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Pyridine-Decorated Carbon Nanotubes as Heterogeneous Metal-free Catalysts for Mild CO_2 Reduction to Methanol with Hydroboranes

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Exploiting carbon dioxide for the production of chemicals and fuels is one of the hottest topics of current sustainable catalysis. On this ground growing interest is devoted to the conversion of carbon dioxide to methanol regarded as a valuable alternative energy source. Unfortunately, CO_2 chemical inertness and thermodynamic stability make its reduction difficult. Many reducing agents in combination with transition metal-based heterogeneous catalysts have been employed successfully for the conversion of CO_2 into products of added value but, on a longer term vision, a sustainable, cheap and environmentally benign alternative is offered by metal-free catalysts. Recently, a variety of organocatalysts operating under *homogeneous* conditions has emerged for CO_2 reduction into valuable products.[1] In particular, N-heterocycles featured by N-[2] or C-[3] basic sites have shown remarkable activity in CO_2 hydroboration to methanol. Following our experience on metal-free N-decorated carbon nanomaterials (N-CNMs) successfully employed in several key catalytic transformations,[4] pyridine-decorated carbon nanomaterials have been tested for chemical reduction of CO_2 to methanol with different hydroboranes. Catalyst recycling tests have also been run showing complete recovery of its performance even after several runs. With turn-over numbers close to those claimed for other metal and metal-free homogeneous catalysts of the *state-of-the-art* and its effective re-use in catalysis, pyridine-decorated carbon nanomaterial candidates as a heterogeneous benchmark for this process. In addition, a hydroboration mechanism has been proposed on the joint basis of experimental data and *ab initio* simulations, suggesting the key role of the carbon nanotube carrier as an electronic reservoir for the dangling pyridine active arms. The latter point paves the way to the future exploitation of our catalyst technology towards more sustainable leaf-like photoelectrocatalytic cells[5] for CO_2 conversion into products of added value.

Parole chiave: Functionalized carbon nanotubes, CO_2 reduction, Metal-free catalysis

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Solid State NMR Spectroscopy and ^{1}H Relaxometry for a Multi-Scale Investigation of Innovative MgO-Based Cements

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In the last years, MgO-based cementitious materials have attracted great interest because of the low CO_2 emissions associated with their production and especially for applications requiring relatively "low" pH of the cement pore solution, such as nuclear waste containment [1]. The binder phase of MgO-based cements is magnesium silicate hydrate (M-S-H), the amorphous phase that forms from the reaction of MgO with a source of silica and water. Although the structure and nature of M-S-H have been investigated [2-3], a full comprehension of properties, such as the hydration kinetics, the nature of the hydrated products and their multi-scale structure and organization, is still lacking. The investigation of these properties, as well as the research for new formulations with improved performances, is fundamental to achieve the industrial breakout of these materials. In this work we have combined Solid State NMR spectroscopy (SSNMR) and ^{1}H relaxometry to obtain a detailed multi-scale description of novel MgO-based cements prepared by hydration of MgO and fumed silica (SiO_2) and of mixed formulations containing MgO/SiO_2 and Portland cement. A ^{29}Si SSNMR investigation on samples freeze-dried at different hydration times allowed us to obtain quantitative information on the nature and structure of the binder phases at the nanometric level, as well as on their formation kinetics [4]. The analysis of ^{1}H T_2 and ^{1}H T_1 obtained by means of Fast Field Cycling relaxometry on cement pastes during their hydration provided a description of the state of water and of the evolution of the solid phases [5].

Parole chiave: NMR, cements, nanoscale, structure, dynamics, water

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Caratterizzazione di Materiali Innovativi per Applicazioni Strutturali

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Il lavoro presentato ha lo scopo di illustrare le attività di ricerca svolte dal gruppo di "Caratterizzazione di materiali innovativi per applicazioni strutturali", presso la sede di Milano dell'Istituto ICMATE-CNR. Tali attività sono indirizzate principalmente alla caratterizzazione meccanica e microstrutturale di materiali innovativi utilizzati nel campo dell'ingegneria, in particolare per le applicazioni a elevate temperature, e alla modellizzazione del loro comportamento meccanico mediante lo sviluppo di equazioni costitutive, basate su modelli fisici di deformazione e danno. Come conseguenza di numerosi programmi di ricerca svolti in ambito nazionale e internazionale con il mondo industriale ed accademico, il gruppo ha maturato una notevole esperienza nell'esecuzione di prove di creep, fatica meccanica e termomeccanica, rilassamento degli sforzi, propagazione di cricca, trazione, nonché nell'analisi dei risultati sperimentali e nella correlazione fra le caratteristiche meccaniche delle leghe studiate e la loro microstruttura.
Le tematiche affrontate sono quindi relative ad un'ampia gamma di leghe utilizzate in impianti per la produzione di energia, in applicazioni aeronautiche e nell'industria manifatturiera.

Parole chiave: leghe metalliche, caratterizzazione meccanica, microstruttura, produzione di energia, manifatturiero avanzato

Amphiphobic Coatings for Antifouling in Seawater Environment

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Amphiphobic materials represent a relatively young emerging field achieving growing interest as innovative solution, meeting technological and ecological aspects, taking into account the limitations imposed by international laws in terms of environmental protection.
In this work different coatings dedicated to the marine environment, showing highly water and oleo repellence, have been compared for applications and characterized and tested both in laboratory and field conditions, considering investigations in real seawater as crucial to evaluate the behaviour of such surfaces in complex environments not reproducible in laboratory.
Also preliminary tests for wearing, thermal stress and durability have been carried out in order to study amphiphobic systems for other applications related to the marine environment.

Parole chiave: antifouling coatings, marine environment, anphiphobic

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RITMARE (La Ricerca Italiana per il Mare) Flagship Project

Wettability of Transparent YAG ($Y_3Al_5O_{12}$) by Molten AgCuTi Alloys and Joining Study of YAG/AgCuTi/Ti_6Al_4V Systems

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The aim of the research is to find a promising filler alloy/metal to be used in YAG-Ti6Al4V joints .
The wettability and the reactivity of the system is studied at different temperatures allowing to define the interfacial phases formed on the ceramic substrate. The low contact angle values obtained ensure very good (at 950°C) and fair (at 850°C and 820°C) wettability conditions. A significant reactivity occurred at the solid–liquid interfaces, with the formation of new phases. The role of the activity of Ti in determining the interactions between the brazing alloys and the YAG substrate has been analyzed by CALPHAD method. All these phases were identified by the recalculated Ag–Cu–Ti phase diagram and were confirmed by SEM and EDS analyses. The obtained good wettability and the maintained transparency of the YAG made possible the production of brazed YAG/Ti6Al4V optical windows to be used under extreme conditions.

Parole chiave: wetting, joining, optical windows

Riferimenti:

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Design of Metal-Ceramic Interfaces for High Temperature Applications

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This poster is aimed at summarizing the main research lines of the metal-ceramic group at ICMATE-GE.
A description is presented of the relevant theoretical and experimental aspects of wettability studies at high temperatures, together with the results used to derive chemical and structural information on the solid-liquid interactions.
The study of metal-ceramic interfaces at high temperature is fundamental to understand the basic mechanisms of materials stability, reactivity and integrity, and it is also functional to obtain all the necessary input data for processes such as production of metal-ceramic composites and joints, casting of special alloys and so on.
The design and optimization of these processes require expertise in various research fields from basic science to application, principally: 1) Thermodynamic, kinetic and atomistic modeling; 2) Interfacial science; 3) Microstructural characterisation; 4) Mechanical testing and 5) Manufacturing process simulation.
Recent systematic studies, referred to the interactions of various liquid alloys with advanced ceramics, and ceramic matrix composites, are presented. These studies address both basic (wettability, interfacial tension, phase equilibria determination) and application (joining, casting) aspects. In particular, a special attention is paid to elucidate the role that dissolution, chemical reactions, additions of active metal elements to the molten matrix have in the wetting process and in the solid-liquid adhesion.
The utilization of phase diagrams is shown, as one of the most powerful tool to design the best alloy compositions for the optimization of joining (brazing) processes, and for the production of metal-ceramic composites.

Parole chiave: interfaces, brazing, wettability

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Surface Engineering of SiC_f/SiC Composites by Selective Thermal Removal: Evaluation by Surface Analysis and Wetting Tests

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One of the relevant results obtained in the European project ADMACOM (Advanced manufacturing routes for metal/composite components for aerospace), funded from the European Union's Seventh Framework Programme FP7 2007-2013, is reported.
The design of interfaces by surface modification and engineering coupled to suitable joining materials and technologies is a key parameter in joint manufacturing. Selective removal of material from the surface, that can be carried out on specific phases or on parts of the material, has been investigated as an efficient way to increase of the joined specific surface, the infiltration of the joining material in the modified surface, and an expected increase of the joint strength of SiC_f/SiC composites.
In this work, SiC_f/SiC "brush-like" surfaces were obtained by using a thermal treatment under argon flow at 1450°C that led to the selective thermal removal (STR) of the SiC fibers. The effectiveness of the STR was evaluated by surface analysis and high-temperature wetting tests. As observed through 3D confocal microscopy, the thermal treatment led to a selective removal of the surface fibers so that the specific surface increased.
Wetting tests were performed using a Ag-Cu-Ti brazing alloy. The STR led to a negligible increase of the contact angles, which ranged from 16° to 21° for as received composites and increased to 28° for composites after STR. Microstructural observations showed that the brazing alloy perfectly adhered to the brush-like surfaces giving a mechanical interlocking expected to enhance the strength of the joint.

Parole chiave: Brazing, SiC composites, aerospace, wetting.

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High Power Impulse Magnetron Sputtering Coatings for Harsh Environments

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The need for materials with special functionalities is particularly felt in forefront domains. In the field of refractory hard compounds, the development of new materials is restricted by various metallurgical criticisms, which force the use of sophisticated and expensive production methods. The film deposition from vapor phase enables the fabrication of new materials, avoiding problems connected with liquid phase formation and/or machining. Thin coatings are designed and applied to modify the surface properties of bulk materials, thus protecting them from mechanical, physical or chemical damages.

In this study, an investigation on protective films for harsh conditions, produced in CNR-ICMATE laboratories is presented. Thin films were deposited by High Power Impulse Magnetron Sputtering (HiPIMS) which is an emerging Physical Vapor Deposition (PVD) technology, combining advantages of magnetron sputtering with several forms of energetic deposition of films (such as Ion Plating and Cathodic Arc Deposition). Used multimagnetron system can work in different hybrid configurations combining HiPIMS with DC, pulsed DC and RF Magnetron Sputtering supplies.

HiPIMS process produces an ultra-dense plasma, which leads to a very high ionization degree of the sputtered material with respect to conventional magnetron sputtering techniques. The growth of ultra-dense coatings is promoted, with enhanced adhesion, in particular for complex-shaped surfaces, improved toughness, reduced columnar structure, residual stress and deposition temperature. Moreover, HiPIMS includes the possibility to deposit alloy compounds, multilayer compositions and structures, and the ability to obtain functionally graded coatings.

Numerous applications were identified for the coatings with such improved properties: high temperature stage of gas turbine engines, internal combustion engines, structural steels operating in heavy liquid metals (HLMS). Several coatings (TiAlN, TaAlN, TaN and MoN) were deposited on innovative and traditional materials, as γ-TiAl, martensitic stainless steel (T91), AISI 304 and AlSi. Depending on coating specific application, appropriate characterization techniques were selected to investigate films properties. Morphologies, compositions and structures of the films were analyzed by FIB, SEM, EDS, XRD, XPS and optical microscopy. The mechanical and tribological characterization included hardness measurements by nano-indentation, adhesion evaluation by scratch tests, wear and friction tests under different loading conditions.

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Fe-Mn-C Alloys for Biodegradable Metallic Implants: Influence of Mn Content

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In recent years, biodegradable metals (BMs) for developing temporary vascular and osteosynthesis devices are gathering an increasing worldwide interest. BM should offer appropriate mechanical properties, sufficient X-ray visibility, especially for small devices, and suitable cytocompatibility. Several BM systems were proposed, respectively based on Mg, Zn and Fe. Fe-based alloys have often a consistent amount of Mn. The effect of this element is evident from a mechanical, electrochemical and biological point of view. In this work, Fe-Mn-C alloys, with different Mn contents, were produced by casting; the properties of these alloys were studied, to understand the effects of Mn, microstructural and surface condition states on the degradation behavior in modified Hanks' solution (MH).
The characterization techniques used for the study of the alloy structure, corrosion behaviour and surface morphology were X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDXS), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Two kinds of degradation products were investigated, those formed during the test and collected at the vessel bottom and those detached from the surface after ultrasounds cleaning.
The amount of Mn in the alloys affected not only the corrosion rate of the alloys, but also the degradation morphology and the formation of degradation products. The degradation rate slightly decreased because of the formation of a stable layer of $MnCO_3$ on the metal surface, highlighted by XRD; this layer was more evident for alloys with a higher Mn content.

Parole chiave: Biodegradable alloys – Fe base alloys

Studio e Caratterizzazione di Nanoparticelle e loro Depositi Prodotti in Fiamme

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Una dell'attività di ricerca portata avanti presso l'ICMATE di Milano riguarda la sintesi di nanoparticelle prodotte in fiamma e la loro caratterizzazione. In particolare cambiando il combustibile di alimentazione della fiamma in studio è possibile produrre nananoaprticelle carboniose o ossidi inorganici. Il vantaggio di utilizzare la fiamma come reattore sta proprio nella possibilità di controllare il processo di sintesi, nel senso di poter controllare la cinetica del passaggio dalla fase gas a quella solida. Lo scopo è quello di produrre nanoparticelle con caratteristiche controllate, quali dimensione, cristallinità e morfologia. Inoltre cambiando opportunamente la stechiometria è possibile cambiare e monitorare la loro composizione.
In questo lavoro sono presentati in particolare due impianti per la produzione di nanoparticelle. Il generatore di nanoparticelle carboniose è alimentato da un combustibile idrocarburo opportuno, mentre le particelle di ossidi sono sintetizzate tramite flame-spray. Entrambi gli impianti sono stati realizzati e caratterizzati presso i nostri laboratori.
Inoltre, nel caso degli ossidi inorganici, l'impianto di flame-spray è accoppiato ad un sistema di deposizione delle nanoparticelle su supporto opportunamente scelto in relazione alla particolare applicazione. Nel lavoro vengono presentati i dati relativi alla sintesi del TiO_2 su supporto di allumina per applicazioni fotocatalitiche. Nanoparticelle e depositi (tal quali o trattati termicamente) sono caratterizzate utilizzando le seguenti tecniche: XRD, SEM-FEG e FT-IR.
Per quanto riguarda le nanoparticelle carboniose, oltre all'applicazioni delle tecniche standard, il laboratorio vanta competenze nell'applicazione di diagnostiche ottiche/ laser che consentono di investigare le proprietà ottiche di questi materiali. In particolare, è oggetto di studio la potenzialità della tecnica di incandescenza indotta da laser nel modificare queste proprietà in modo controllato.

Parole chiave: nanoparticelle, ossidi, flame-spray , proprietà ottiche

Riferimenti:
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Engineering the Self-Assembly of 1D Polyrotaxanes *via* Coordination Chemistry and Supramolecular Tools

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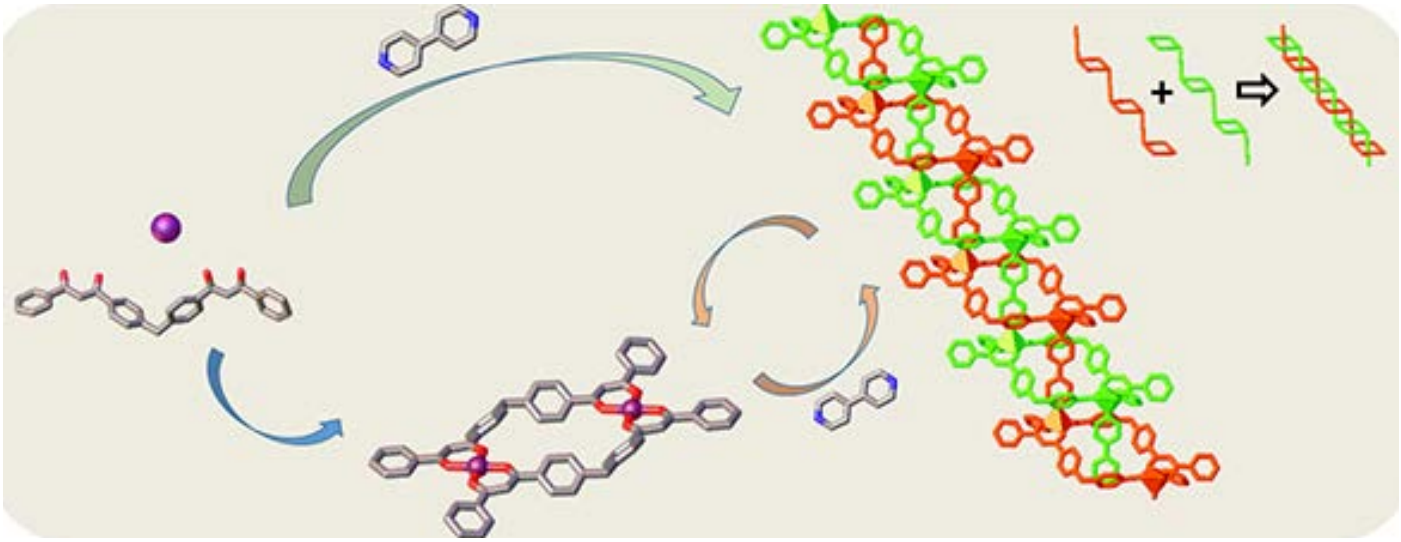
Interest in MIMAs (mechanically interlocked molecular architectures), i.e. molecules that are entangled as a consequence of their topology, is rapidly growing since they are at the roots of molecular machines and applications in various fields such as catalysis, host-guest chemistry, energy harvesting, biomedical applications and smart materials.[1] Metal organic frameworks (MOFs) are another important and well-established class of molecular based materials. PMOFs (Polyrotaxanes MOFs) merge the properties of the MIMAs and MOFs. Here, we describe a rational approach to design and engineering the self-assembly of 1D polyrotaxanes *via* coordination chemistry and supramolecular tools. Metallo-supramolecular boxes and their host-guest properties are used as platforms towards the extended systems. In particular, coordination chemistry allows to assemble the loops of the polyrotaxane motif as well as to connect them through the axle component. Alternatively, the interlocked systems can be supported by π-π interaction.[2] Moreover, by playing with the coordination chemistry of the metal ion we can reversibly tune the self-assembly process of the polyrotaxane architecture.[3]



Key words: supramolecular chemistry; coordination chemistry; host-guest; polyrotaxane; single crystal

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Utilizzo della Lega NiTi Pseudoelastica per lo Sviluppo di un Damper ad Uso Civile

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La lega NiTi equi-atomica appartiene alla classe delle leghe a memoria di forma (SMA) ed è conosciuta per le sue eccellenti e uniche proprietà meccaniche che prendono origine da una transizione termo-elastica del primo ordine tra due fasi solide distinte, martensite e austenite. Questo passaggio di fase consente il recupero di grandi deformazioni in campi di sforzo elevati, e fa sì che queste leghe vengano ampiamente impiegate in applicazioni ingegneristiche avanzate.
In particolare, la lega NiTi in fase austenitica presenta un comportamento pseudoelastico, caratterizzato da un'ampia isteresi termo-meccanica e da un recupero completo della deformazione imposta. Grazie a questa risposta meccanica, la lega NiTi pseudoelastica è adatta a smorzare o prevenire oscillazioni di un sistema fisico, e trova principale impiego nell'isolamento sismico di strutture a terra.
In questo contesto, è stato progettato e realizzato un damper costituito da un sistema complesso di fili NiTi pseudoelastici di differente lunghezza, in grado di promuovere il ricentraggio, la bi-direzionalità della risposta meccanica, la modulazione del tratto elastico.
Test sperimentali standard di trazione sono stati eseguiti al fine di valutare i parametri energetici chiave: la capacità di damping globale, l'energia dissipata ad ogni ciclo e il carico massimo attenuato. Questi test sono stati eseguiti sia in condizioni quasi-statiche [1] sia in frequenza (a 0.5, 1 e 2 Hz per 1000 cicli meccanici) [2]. Parallelamente è stato implementato un modello numerico uniassiale fenomenologico in grado di predire la risposta di sistemi pseudoelastici più complessi [1, 3].

Parole chiave: NiTi, pseudoelasticità, materiali avanzati, damper

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Porous Materials from Particle-Stabilized Liquid Foams

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A preparation method based on gel casting of particle-stabilised liquid foams, followed by a thermal treatment, has been developed to prepare porous materials (solid foams).
The stability of the precursor liquid foam is ensured by the segregation of particles at the liquid-air interface. To this aim, surfactants are utilised to tune the hydrophobicity of nanosized particles dispersed in an aqueous phase. This peculiarity makes the methodology adaptable to virtually any type of particle, by choosing a proper surfactant.
The physicochemical interfacial and bulk properties of the initial dispersions are fundamental to establish the structural and mechanical properties of the final solid materials. The analysis of these properties is therefore utilized to drive the formulation and the processing.
This method has been utilized so far to prepare different types of ceramic and carbonaceous materials [1-3], such as titania, alumina and active carbon foams, characterized by different degrees of porosity and morphology (f.i. open cells). These materials present in particular a hierarchical porosity, from the nanometric to the millimetric scale: a feature particularly useful in applications related to catalysis or adsorption.
Important steps have also been done for adapting the methodology to the preparation of multicomponent materials, where some of the particle species are selectively segregated at the surface of the cells during the formation of the foam. That in order, for example, to obtain materials characterised by adequate mechanical resistance, coupled with specific surface functionalities. Proofs of concepts have been already given for system containing mixes of nanometric silica and titania particles.

Parole chiave: porous materials, solid foams, nanoparticles, particle-stabilised foams

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The Use of Nanoparticles in the Enhancement of the Tribological Properties of Lubricating Oils

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Superior tribological properties of nanolubricants have been recently well established for conventional oils, and enhancing the tribological performance of lubricants with nanoparticle additives is currently an active area of research. Recently scientists used nanoparticles in different tribological systems and nanolubricants have been widely studied as an alternative solution to conventional lubricant oils, since they allow obtaining significant reduction of friction and improvements of load-carrying capability. The action of nanoadditives reduces friction and wear on surfaces that operate in sliding contact with each other. Of particular interest are graphene and carbon based nanomaterials, such as Carbon Nanohorns (CNHs) and Carbon Nanotubes (CNTs). CNHs have been the subject of numerous studies due to their unique morphology and wide ranging properties of graphene, including chemical stability, low surface energy and high thermal and electrical conductivity. However, limited investigations were carried out on their tribological and anti-wear properties.
In addition, nanofluids containing lyotropic mineral particles responsive to external magnetic fields can combine the fluidity and anisotropy of liquid crystals with the specific magnetic and transport properties of dispersed mineral compounds. Goethite (α-FeOOH) based colloids are mineral liquid crystals exhibiting a peculiar magnetic behavior, which allows tuning their properties by the application of an external magnetic field. The tribological performance of α-FeOOH has been rarely reported in literature. As goethite is a chemically reactive material, it represents a suitable functional additive in lubricants to promote the formation of a protective tribofilm during the rubbing process, because of tribo-chemical reactions, especially under severe working conditions, such as mixed and boundary lubrication.
Herein, a summary about last studies carried out on different nanolubricant systems is presented. The enhancement of tribological properties of nanofluids containing CNHs and goethite nanorods is reported, that deals also with the differences in anti-friction and anti-wear capabilities of these systems, due to a variation of the surface topology of the substrate, in terms of roughness, operating temperature and nanoparticle morphology. The action mechanisms of different dispersed nanoadditives have been deeply investigated.

Biomedical Applications in Neuromuscular Rehabilitation: Materials, Interfaces, Sensors and Designs

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In gruppo del CNR ICMATE di Lecco si occupa della sintesi, lavorazione, test delle leghe Shape Memory Alloys (SMA) che rappresentano una valida ed interessante classe di materiali con particolari e specifiche caratteristiche come la pseudoelasticità, la memoria di forma indotta dalla temperatura (SME), isteresi meccanica e termica, che li rendono validi candidati per numerose applicazioni in differenti ambiti. Il gruppo di lavoro, sotto la responsabilità dell'Ing. Pittaccio e composto dagli ingegneri Lorenzo Garavaglia (analisi dati e progettazione di set-up sperimentali per studio e applicazione dei materiali), Fabio Lazzari (progettazione di schede elettroniche per controllo materiali e dispositivi) e Iacopo Romanò (studio di elementi di interfaccia per scansione e stampa 3D per la combinazione di differenti materiali), si occupa in particolare delle applicazioni biomedicali delle SMA; sfruttando le molteplici caratteristiche di questa classe di materiali il gruppo negli ultimi dieci anni ha collaborato attivamente con numerosi centri clinici al fine di sviluppare dispositivi dinamici meccanici e meccatronici per la soluzione di problemi clinici di difficile gestione nell'ambito della riabilitazione neuromuscolare e delle neuroscienze.
Questo lavoro presenterà i molteplici risultati ottenuti nell'ambito della neurologia e riabilitazione neuromuscolare. Dall'obiettivo principale che risiede nella progettazione e costruzione di dispositivi che forniscano campi di forze dinamici viscoelastici e non statici e quindi fisiologicamente più simili a quelli del sistema biologico, rispetto ai sistemi classici in uso, l'interesse del gruppo si è focalizzato anche sulla necessità di personalizzare le funzioni, di creare dispositivi leggeri, indossabili e compatibili con le moderne tecniche di indagine diagnostica e la necessità di favorire la riabilitazione a casa. Un ulteriore ambito di sempre maggiore interesse per il gruppo, a supporto della progettazione ed uso di dispositivi basati sulle leghe SMA, è dato dallo sviluppo di sensori elettronici per la valutazione cinematica delle performance dei dispositivi, a fianco dell'integrazione con nuovi materiali morbidi e compositi per coniugare differenti funzioni e massimizzare il comfort, anche grazie allo studio delle superfici anatomiche e quindi il miglioramento e funzionalizzazione delle interfacce tra il paziente e il dispositivo. In tutti questi ambiti e conseguenti applicazioni, lo studio e l'ottimizzazione delle caratteristiche dei materiali risulta di primaria importanza.

Parole chiave: leghe pseudoelastiche, SMA, riabilitazione, ortesi, materiali funzionali, disturbi del movimento, sensori cinematici, ricostruzione e funzionalizzazione di superfici anatomiche.

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CVD Techniques for Surface Functionalization: ALD Potentiality for Long-Range Periodic Structures

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The surface of a solid material and the regions closest to it represent the 'element of dialogue' with the surrounding environment, so conditioning the physical and chemical properties of the material itself. In this context, Material Science is fundamental to properly functionalize the material surface through a suitable bottom-up approach in order to induce a targeted behavior. Chemical Vapor Deposition (CVD) is an attractive technique for the synthesis of opportunely designed nanostructured thin films. The possibility to modify several physical and chemical growth parameters makes CVD a challenging process to tailor material composition, microstructure, and morphology, so influencing the final functional properties.
In particular, Atomic Layer Deposition (ALD), a recent variant of CVD process, is a powerful and unique technique which allows the deposition of high quality thin films with atomic level control of composition and thickness.
The capability to produce periodic metal oxide structures with both a long range order and a good control of dimension at micro- and nano-metric level is of great scientific interest. These surfaces, thanks to their high surface-to-volume ratio, may find wide application in processes based on surface reactions, such as heterogeneous catalysis, sensors and photovoltaics. In fact, although structuring micro- and nano-materials may also be obtained with conventional templating and lithographic techniques, an alternative and strategic approach is found exploiting the self-assembly of polymeric materials (to set the template patterns up) combined with the ALD process (to conformally cover the polymeric templates).
Here, a case study is reported in order to show the ALD potentiality by focusing the attention on the optimization of hybrid organic-inorganic methodology to prepare 2D-microporous TiO_2 with honey-comb (HC) morphology. The hybrid methodology first employs the preparation of a polystyrene template with a specific pattern, which is later used for the subsequent deposition of TiO_2 via ALD at low temperature. Finally, high temperature post-deposition thermal treatments on PS/TiO2 composite material is carried on in order to decompose and extract the PS templates and in the meantime to crystallize TiO_2 in anatase phase, maintaining the HC structure.

Keywords: CVD, ALD, functionalization, periodic structures, metal oxides.

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Graphene-Based Complex Porous Structures: Anisotropic Aerogels Produced by Freeze-Drying Approach

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Graphene-based aerogels exhibit excellent properties, such as low density, high conductivity, outstanding adsorptive property. However, aerogels are mechanically fragile and show poor resilience, which limit their applications. In this work, a novel complex structure with anisotropic electrical conductivity was designed based on open cell polyurethane foams (PUF) and reduced graphene oxide (rGO)/chitosan (CS) aerogel. The lightweight, highly porous, electrically conductive rGO/CS aerogel was formed in-situ within the PUF porous structure via unidirectional freeze-drying technique. As an integrated structure the aerogel was mechanically supported by the elastic PUF scaffold. However the conductive 3D network constructed by aerogel offered a robust conductive network throughout the whole material. Therefore this structure possess many unique features, such as good mechanical properties, excellent electrical conductivity and outstanding piezoresistive properties. To enhance the interface bonding, the PUF surface was coated by an rGO coating layer through liquid phase deposition process. The influence of rGO coating layer on the mechanical and electrical properties was investigated. The electrical properties in the parallel and transverse directions of aerogel growth are reported. This study provides a novel alternative approach to preparing high performance polymer nanocomposites with potential application prospects in many fields, including wearable sensors, catalyst carriers and adsorbent materials.

Parole chiave: Graphene Oxide, Chitosan, Freeze-drying, Aerogel

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Antibacterial Finishing for Textiles

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Antibacterial textiles have obtained increasing interest from both academic research and industry because of their potential to provide better quality life and safety benefits to people [1]. Textile products are prone to host micro-organisms whose proliferation is responsible for diseases, unpleasant odors, color degradation and deterioration of fabrics [2]. Antimicrobial finishes are used in many textile products, such as sportswear, outdoor apparels, undergarments, shoes, furnishings, upholstery, hospital linens, wound care wraps, towels and wipes. Other applications are envisaged for antibacterial filter applications (biotechnology processes, water purification, clean rooms, operating theatres, domestic appliances).
Different approaches for the production of antibacterial fabrics have been developed using natural biocides and polymer biocides with the aim of reducing the leaching of biocidal agents to the environment.
One consists in the modification of cotton fabrics with natural small molecule biocides (e.g., citric acid) bind to fiber surface. An other approach involves the deposition of chitosan followed by UV-curing on fabrics. The last method deals with *in-situ* polymerization on fibers and fabrics of a positively charged conjugated polymer (i.e., polypyrrole). The treated fabrics showed excellent (>97%) antibacterial properties against both Gram-negative and Gram-positive bacteria following standard test methods (AATCC 100, ASTM E 2149-01).

Parole chiave: antibacterial textiles, citric acid, chitosan, polypyrrole

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Electrospun Keratin-based Nanofibers for Biomedical and Environmental Applications

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Electrospinning is a simple method to produce nanofibers with high specific surface [1]. Keratin is a biocompatible and biodegradable protein extracted from wool, which can be electrospun pure or in blend with other polymers, such as polyamide [2]. It supports fibroblasts and osteoblasts growth. Moreover, nanofiber-based filters can remove small-sized particles and keratin nanofibers can absorb heavy metals and dyes from water, and VOCs from air.
In biomedical applications, pure keratin nanofibers was applied as bio-finishing to functionalize titanium surfaces of dental implants [3]. The aim is the improvement of soft tissue adhesion avoiding epithelial down-growth and bacterial infiltration on the collar. Keratin nanofibers were found to greatly improve fibroblast cells growth already at 24h. In bone regeneration, nano-hydroxyapatite (HAp) was used in composite electrospun keratin-based nanofibers. Water was used as solvent to produce HAp/keratin-based composite nanofibers. The nanofibers have been tested for osteoblasts cells growth, showing biocompatibility by cell viability assay. Moreover, antibacterial keratin-based nanofibers were produced by the addition of a protein-complex containing Irgasan, as a model biocide [4]. The material has a slow release with a very high antibacterial activity after 24 h.
Air pollution and water contamination are severe environmental issues. The discharge of polluting wastewater harms the aquatic life, adversely affects human health and limits water resources. New water filtration systems based on electrospun nanofibers have been proposed. In addition, composite nanofibers embedding functional nanoparticles (i.e. TiO_2, silver) allow the depuration of water from pollutant compounds and bacteria [5].

Parole chiave: electrospinning, nanofibers, keratin, biomaterials, filtration.

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Patterning and Self-Organization in Confinement: an Efficient Via to Enhance the Functional Properties of Materials.

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Functional properties of materials depend on their chemical structure as their assembly and spatial distribution at the solid state; the combination of these factors determines their properties and consequently, their technological applications. By controlling the assembly processes and the spatial distribution of the resulting structures, functional materials can be guided to technological and specific applications[1]. We considered the principal self-organizing processes, such as crystallization dewetting and phase segregation. Usually, these phenomena, compromise the technological applicability of many materials, however, sometime, they can be transformed in opportunity by using an appropriate processing[2]. In particular, we focus our attention on the confinement effect achieved by stamp-assisted deposition for controlling size, positions of material assemblies and in some cases the chemistry, giving to the materials new chemical/physical functionalities[3]. We review how spontaneous self-organization processes can be depressed or enhanced by exploiting the spatial confinement imposed by stamps in crystallization dewetting and supramolecular aggregation. We discuss how the crystalline order and orientation can be controlled by confinement, including the partial control of polymorphism and different crystal orientation in patterned thin film. How partial wetting and dewetting can be advantageously exploited by confinement[4] and the confinement effects in chiral aggregation. Moreover, we highlight how physical/chemical properties of soluble functional materials can be driven in constructive ways, by integrating them into operating technological traditional and new devices.

Parole chiave: Unconventional nanofabrication, materials technology.

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Organic Spintronic Devices: Transport Regimes and Applications to Neuromorphic Computing

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Despite the extensive research efforts devoted to the understanding of spin transport in organic semiconductors, key results, such as the Hanle effect, are still missing[1], [2]. Many of the results in this field were obtained with the organic semiconductor (OS) tris(8-hydroxyquinoline)aluminum (Alq3); surprisingly little systematic work has been carried out on the temperature, thickness and voltage dependence of the resistance of organic spintronic devices made from this material. We reviewed the data available from the literature and we have contrasted it with the data collected in our laboratory. We have identified two distinct sets of devices, one with low resistance that shows spin valve magnetoresistance, and one with high resistance, with no magnetoresistance; the set a specific device belongs to does not depend on its thickness. All the surveyed Alq3-based spin valves from the literature, as well as those made in house, belong to the former set. After rescaling for the active area of the devices in this set, we have found no dependence of the resistance on the thickness of the OS.

The voltage and temperature dependence of the high resistance devices followed accepted models for conduction in organic solids, while the thickness dependence followed it more loosely. As expected, at low applied voltages, the behavior transitioned from ohmic at room temperature, due to thermally activated carriers, to space charge limited at 100 K, since at this temperature only injected carriers participate in charge transport.

To understand the low resistance devices, that show magnetoresistance and resistive multistability we have expanded on the impurity band model introduced by Yu[3]. In our devices we envisage oxygen to be the impurity[4] and bistability is attributed its migration within the organic semiconductor/AlOx bilayer. This model provides a comprehensive explanation of the phenomena observed in the low resistance devices, including the interplay between the resistive state and the magnetoresistance.

These devices can be used for neuromorphic computing: with positive voltage pulses of fixed duration and amplitude it was possible to increase gradually the conductance of the device, while with negative voltage pulses it was possible to decrease it. This type of synapse can be used in several types of neural networks, from a simple single layer perceptron to spiking neural networks. The presence of magnetoresistance adds a unique tool to effect parallel, selective changes on the weight of synapses. This possibility provides a novel tool for neural network training.

Parole chiave: organic spintronics, spin transport, neuromorphic computin

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Nanostructured Silicon Nanowire and Electrospun Nanofibre Polymer Interfaces Induce Neural Cells Molecular and Functional Differentiation *in vitro*

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Astrocytes are one of the most numerous types of cells in the central nervous system (CNS) which play crucial role in the maintenance of cerebral homeostasis as well as in the modulation of synaptic activity. Growing evidence indicate also the causal role of astrocytes in several neurophathologies and disease. In this view there is an increasing demand of *in vitro* models enabling the study and the manipulation of astrocytes ion channels and aquaporins. One major challenge in the study of astrocytes membrane channels *in vitro*, is that their expression pattern does not resemble the one observed *in vivo*.
In this view attention is paid in developing novel nanostructured biomaterials able to modulate the astrocytes molecular and functional properties *in vitro*, that might help to generate significant knowledge in CNS. To address this issue we investigate on the effect on primary rat cortical astrocytes growth and physiology of innovative nanostractured material interface based on inorganic gold coated silicon-nanowires (Au/SiNw) and on electrospun nanofibers made of organic polymers polycaprolactone (PCL).
By means of cell viability assays we found that Au/SiNw as well as PCL electrospun nanofibers promote strong adhesion of astrocytes without need of additional coating with values comparable to those obtained by using glass coverslips treated with Poly-D-lysine. Optical and fluorescent imaging at different time point revealed that nanostructures promote modification of astrocytes morphology. Scanning Elcctron Microscopy and Atomic Force Microscopy confirms the capability of astrocytes to responds to substrates topography. We found that interfaces can promote astrocytes differentiation and three dimensional growth and by promoting endfeet sprouting from the cell body lining and enveloping the interface nanostructure. The differentiation is not due to gliotic reaction, as GFAP values are unchanged respect to the control. Also, confocal imaging revealed that PCL nanofibre alignment promotes astrocytes growth and orientation along the fiber with induction of F-actin fibre alignment and vinculin polarization. Finally, by whole-cell recording patch-clamp, the eletrophysiological properties of the cells have been characterized, revealing promising features in the expression of ion conductance resembling those expressed by astrocytes in vivo. Our model might be relevant for neuroscience as well for neuroregenerative medicine and neural engineering. Sponsored by AFOSR projects ASTROMAT, FA9550 16 1 0502; ASTRONIR, FA9550-17-1-0502.

Parole chiave: biomaterials, glial cells, molecular and functional characterization

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Keratin Technologies for Advanced Drug-Delivery Systems

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Keratin is the major component of feathers, hair, wool, nails and horns and is one of the most abundant non-food protein. Keratin is characterized by high sulphur content (> 3% wt) compared to other proteins such as collagen or fibroin. Food industry, especially the meat sector, produces more than 40 millions tons/year of keratin wastes and their disposal represents an industrial problem since incineration is extremely inefficient (keratin is self-extinguishing) and polluting (sulphur compounds released). Moreover, the accumulation of keratin-rich waste in the ecosystem exacerbate landscape degradation as well as soil and groundwater pollution [1]. Among keratin sources, wool fibers are constituted by a multi-cell structure composed of about 95% wt of non-toxic keratin proteins which are bioresorbable and are able to facilitate cell adhesion and proliferation due to the presence of cell binding motifs Gly-Asp and Leu-Asp-Val. Wool keratins are therefore promising biomaterials for biomedical applications, especially for wound healing, tissue engineering and drug delivery.
We developed a prototype plant for extracting high molecular weight keratin (45-60 kDa) from wool, allowing to obtain a biomaterial with exceptional physicochemical properties since it can be processed in different kind of molecular scaffolds (*e.g.* nanoparticles, hydrogels, films, nanofibers) and can also efficiently incorporate hydrophobic and hydrophilic molecules such as drugs. In addition, the morphology of these keratin-based materials can be finely tuned to meet specific requirements of degradation and drugs release profiles [2].
We present here an overview on the **recent advances of keratin nanoparticles as pH-responsive carriers of anticancer drugs and keratin/hydrotalcites hybrid patches as carriers of anti-inflammatory drugs**. In particular, we will show the effects of keratin nanoparticles on doxorubicin release profiles and their efficacy towards breast cancer cells, as well as the effects of the composition and morphology on the stability of the keratin-based patches and their diclofenac release profiles.
Finally, this communication will be the occasion to introduce **KerLine Srl, a spin-off company of CNR** founded on June 2017, focused on the development of a demo-plant for the high molecular weight keratin extraction and on the manufacturing of technology provision of keratin-based biomaterials for different market sectors including: high-end cosmetics, advanced medications and pharmaceuticals.

Parole chiave: Keratin, Hydrotalcites, Nanoparticles, Nanofibers

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Biomimetic Graphene for Enhanced Interaction with the External Membrane of Neural Cells

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Graphene oxide (GO) is a highly versatile material, it can be easily dispersed in water media and functionalized/grafted through standard and well consolidated synthetic methods.[1] In the field of neuroscience, the interaction of GO with neural cells is widely studied with the aim at engineering graphene-based medical devices able to transduce neural signal or for neural imaging and optogenetics applications.[2]

Biomaterials targeting nervous system must interact properly with neuronal cells but also with non-neuronal cells, called astroglial cells. Adverse interaction between biomaterials and glial cells could induce an inflammatory reaction ultimately leading to neuronal death at the implant site.[3]

In this work, we describe the synthesis and characterization of a functionalized GO with a synthetic phospholipid (GO-PL). Phospholipids (PLs) are indeed the main structural component of cell membranes and they play a crucial role in the intracellular signaling. GO-PL was employed as substrate for astroglial brain cells. We demonstrate that the as-prepared composite increases the adhesion of the cells with respect to standard glass-coated substrate or non-functionalized GO.

Parole chiave: graphene oxide, astrocytes, biomaterials, phospholipids

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Eco-Sustainable Polysulfone Composites for Environmental Monitoring and Remediation

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Polysulfone is a biocompatible, chemically stable and mechanically robust polymer that can be processed in porous membranes suitable for filtration in biomedical, gas separation and drinking water purification industrial fields.

In particular, polysulfone hollow fibers are widely used for the realization of hemodialysis devices for the removal of large colloids, microbes, and viruses. The preparation of such commercial modules implies the production of scraps (5 to 10% in weight of the total year production) that are considered plastic wastes.
Here, we demonstrate that these scraps can be exploited as starting materials for realizing a new class of polymeric adsorbents (PS-HPG) with combined filtration and adsorption properties toward several organic compounds of environmental concern from water and/or air. The removal efficiency toward volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and compounds of emerging concern (i.e. drugs, personal care ingredients and textile dyes) will be discussed. Moreover, to unravel the full potential of PS-HPG we tested the ability of PS-HPG-based filters for the removal of aerosol nanoparticles. Finally, we describe chemical modification approaches, including graphene based ones, to tailor the surface properties of PS-HPG and to promote selective separation processes.

Parole chiave: polysulfone, graphene oxide, water remediation, adsorption, filtration

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New Frontiers for Liquid-repellent Surfaces: Assessment of their Drag Resistance and Vibration Reduction Properties

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In the last decades, liquid-repellent surfaces have drawn huge interest from both the scientific community and the industry. In fact, a wide range of industrially relevant properties - namely self-cleaning, anti-icing, anti-fouling, anti-friction and many more - derives from the liquid-repellent attitude of materials and components. In the last years, the *Smart Surfaces Group* at CNR-ISTEC has developed an expertise in the design, fabrication and characterization of inorganic or hybrid coatings able to strongly reduce the surface wetting of industrial materials: metals and alloys, glasses, ceramics, natural fibers, polymeric films, etc. Through the choice of suitable deposition methods (dip coating, spray coating, roller printing) and process parameters, the coatings surface chemistry and morphology can be tuned in order to broaden the range of liquids which can be repelled. Being the know-how of materials and processing criteria to *superhydrophobic*, *oleophobic* and *amphiphobic* surfaces rather strengthened, our current work is now eager to explore the further potential of these surfaces, aiming to extend their application range at industrial level in the sectors of i.e aerospace, maritime and naval applications. This approach requires very often to address different scientific competences, equipment and facilities.
The already established collaboration with CNR-INSEAN is allowing to study the underwater behavior of superhydrophobic surfaces. More specifically, ISTEC CNR fabricated large water-repellent surfaces (45 x 30 cm) on aluminum slabs as per two biomimetic approaches, namely the SuperHydrophobic Surface (SHS) and the Slippery, Liquid-Infused Porous Surface approach (SLIPS). CNR-INSEAN, together with Centro per Esperienze Idrodinamiche della Marina Militare (CEIMM) custom-made an experimental setup to assess the materials surface behavior in terms of skin-friction drag resistance and acceleration response. Results showed that SLIPSs provide a remarkable decrease in drag resistance (10-16% reduction in friction coefficient) and in acceleration amplitude at mid-high frequencies (2.5 dB reduction in noise radiation).
These findings, although preliminary, could have huge positive fallout on naval transportation, as they would lead to higher speed, lower emission and increased mission range for underwater vehicles, more reliable operation of sensors, diminished fatigue of pipes and launchers, increased on-board comfort for ship crews and passengers.

Parole chiave:
superhydrophobic, coatings, surface engineering, reduction of drag resistance, vessel vibration.

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Sintering Behavior of Large Ceramic Slabs

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The ceramic industry is currently addressing the production of porcelain stoneware tiles towards larger and larger sizes with different thickness. Novel shaping techniques, together with redesigned manufacturing lines, allow to output slabs from 320x160 cm to 480x180 cm (from 5.1 to 8.6 m^2) with thickness from 3 mm to 20 mm (weight from 35 to over 400 kg). The driving force of this product and process innovation is twice: gain in efficiency and productivity from highly standardized manufacturing plants (towards the digital factory 4.0) as well as commercial return from value added, versatility (offcuts can be tailored on demand from a single slab) and new application fields (e.g., ventilated façades, furniture, substitutes for ornamental stones and wood slabs). On the other hand, the production of such gigantic slabs – matching the standard requirements for porcelain stoneware (water absorption ~0.1% and deviation from planarity <0.5%, among others) – is challenging and the control on deformations taking place during firing turns crucial. Indeed, densification of porcelain stoneware occurs by a complex process, entailing partial vitrification, reactive sintering, and viscous flow of melt in equilibrium with residual minerals (mostly quartz) and newly formed crystalline phases (essentially mullite). The intricate convolution of these phenomena makes porcelain stoneware firing the least known and the hardest to model amongst sintering processes. The CNR contribution to ongoing research projects with industrial partners focuses on in-depth comprehension of the evolution during firing of phase amount and chemistry. Quantitative phase analysis was performed by XRPD with Rietveld refinement and chemical composition of the vitreous phase was calculated by subtracting the contributions of crystalline phases from the bulk composition. The melt physical properties at high temperature were estimated by its chemical composition by using models for magma viscosity. In industrial firing, feldspars melt quickly, while quartz is only partially dissolved at the highest temperature. Once formed, mullite is gradually dissolved, though by a decreasing rate, making the melt increasingly peraluminous. The melt viscosity lowers rapidly up to 1200°C, but tends to slowly increase during soaking. These physical and mineralogical features – not merely predictable by phase diagrams – affect both sintering kinetics and tile deformation at high temperature (*pyroplasticity*). In particular, pyroplasticity depends on both the melt viscosity and the amount of crystals suspended in the liquid phase. Analogously to natural melts, firing deformation could scale with crystals shape and size distribution, which in turn reflect in a complex way the dissolution rate of mullite and quartz into the melt (buffered by the silica oversaturation and strong peraluminous character). Such findings made it possible to draw a phenomenological model of porcelain stoneware sintering, which enables ceramic technologists to improve the design of body composition and processing variables.

Parole chiave: Ceramic, Phase composition, Porcelain Stoneware, Sintering.

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Water Purification with Active Cotton Membrane: Photo- and Photoelectrochemical Treatments in Semi-Pilot Plant

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Semiconductor photocatalytic technology using either UV or solar light has recently come into prominence owing to its mineralization aspects and its advantages as compared to other oxidative processes that require the use of potentially dangerous chemicals or disinfectants. The ProBioType II project, funded by the Italian national program Fabbrica del Futuro, investigated the development and up-scaling of photocatalytic reactors, designed to be downstream modules of chemical plants or more traditional purification systems. This activity meets the need of ISTEC-CNR to transfer to large scale plants the long experience gained in photocatalytic technologies and in the development on nano-TiO_2 based photocatalytic materials[1-4]. The project allowed the up-scaling of a lab-scale pilot plant (1L) to semi-pilot plants with different geometries (6L and 10L), up to a pilot-scale plant (100L). Using UV or visible LEDs irradiation, the degradation of Rhodamine B was used as a probe reaction. In particular, this study is focused on the developments of 10L capacity semi-pilot plant. Several kinds of photocatalytic membranes based on commercial cotton fabric coated with nano-TiO_2 were used within semi-pilot photoreactor and compared. The preliminary test in semi-pilot plant by the standard photocatalytic approach showed very promising results, with photocatalytic efficiencies around 90% within four hours of UV irradiation (Figure 1), and performance conservation even after five complete recycling tests. An implementation of the photocatalytic approach was also pursued in which an additional electrochemical functionality was added to the system employing palladium-doped TiO_2/Ti anodes obtained by thermal oxidation of ASTM Grade 1 titanium mesh (Figure 2). Results show that an increase of the rate of degradation of Rhodamine B can be obtained as compared to that measured with photocatalytic membranes only. The dependence of the RhB degradation reaction rate and degradation kinetics on the type of salts added as support electrolyte was investigated. The electrochemical performance of TiO_2(Pd)/Ti anodes was found to be constant over many four-hour cycles. The proof of concept achieved at pilot scale level, will allow a sound evaluation of environmental impact as well as of other technical feasibilities and costs, pushing the proposed technology towards its commercialization.

Parole chiave: Photocatalysis, photoelectrochemical process, nano-TiO_2 coated textile, semi-pilot plant

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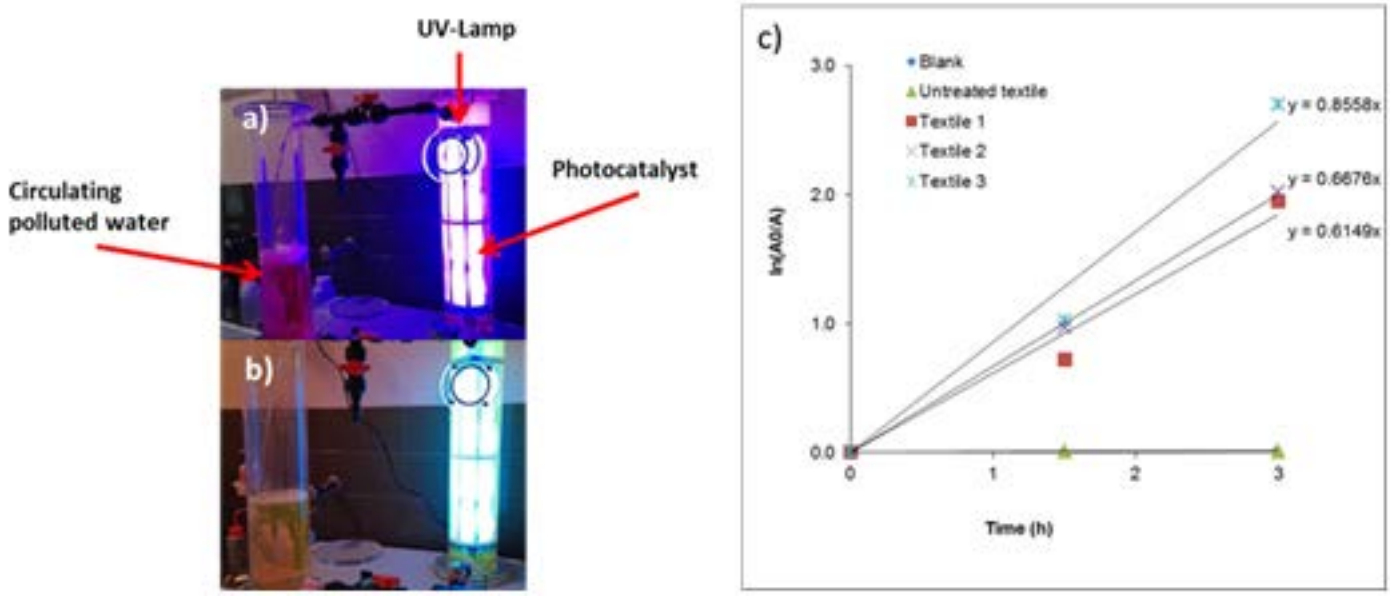

Figure 1. 10L photoreactor containing Rhodamine B treated with nanoTiO_2 supported on textiles and irradiated by UV light. Irradiation time: a) t=0; b) t=3h. c) kinetic constant comparison of different nano-TiO_2 coated textile supports, in 10L photoreactor.

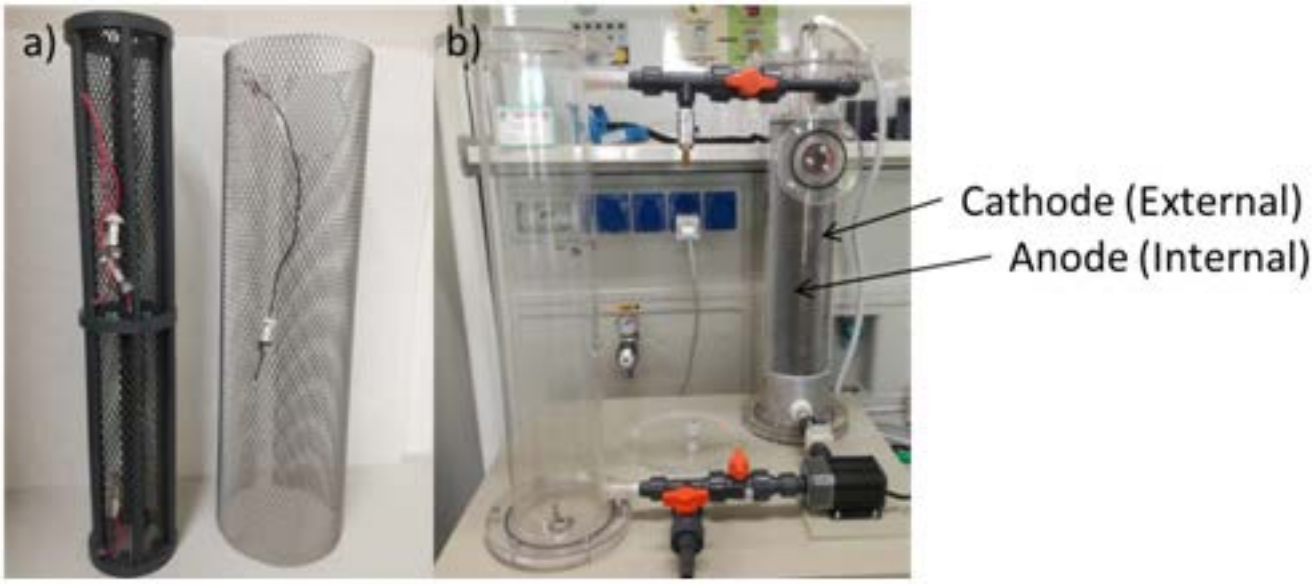

Figure 2. Photograph of a) contacts to anode (left) and to cathode (right); b) insertion of electrochemical apparatus into semi-pilot plant.

Design and Monitoring the Biological Reactivity of Luminescent Nanomaterial

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Nowadays is getting more and more interesting the research focused on the safe use of nanotechnology and nanomaterial design for biological applications, following the principles of Safe by Design and Green Toxicology. Within the great goal to evaluate and control the interaction of nanoparticles with biological targets, we analysed some case studies both in terms of nanoparticles intrinsic properties (such as composition, dimension, superficial area, etc.) and their biological effects, considering as final target the human dermal exposure, selecting a trans-dermal exposure mechanism (Franz cell model) and considering both exposure of workers in a production site and that of consumers wearing textile products.

As first case study, we investigated a silica (Ø 20 nm SiO_2NPs) based nanosol functionalized by cyclometalated Iridium(III) complexes (Ir@SiO_2NPs), that are physically embedded in the silica matrix. We studied the systems both in liquid state and once deposited as nanostructured coating on the cotton textile samples (figure 1). As main interesting result we noticed an improvement of the complex optical properties once introduced in the silica matrix. This phosphorescence optimization promoted the release by the stabilized complex of singlet oxygen (a reactive oxygen species: ROS) once exposed to ambient light at room temperature, causing the occurrence of an interesting antibacterial activity that allowed us to obtain and characterize antibacterial self-marker coated textiles. In order to collect information useful for the human risk assessment of so functionalised antibacterial textile, we followed an exposure model in vitro (ex-vivo) of human skin (Franz cells). ICP-MS analysis results showed that Ir@SiO_2NPs system exhibited a very low adsorption inside the skin samples of donors, the functionalized NPs stopped on the surface, in epidermis layer, without any trans-dermal passage. Furthermore, the presence of phosphorescent complexes allowed to monitor the transport of such nanoparticles through dermal barriers. Performing fluorescent microscopy analysis, we were able to cut-off the skin autofluorescence, focusing on complex emission and obtaining a screen in depth of the first 50 µm of the epidermis. As reported in literature, we could identify in some samples luminescent canals observed in fluorescence tomography, that corresponded to the hair canal inside the bulb. Therefore it is reasonable concluding that Ir@SiO_2NPs potentially released by the textile surface will be stopped in the first layers, moving to the hair bulbs and crowding round without any strong damage against inner layers and the rest of the organism.

These results are actually promising and encouraged the use of Ir@SiO_2 coated textiles as self-markers antibacterial products with high selectivity for bacteria, for which can be predicted a low human skin damage.

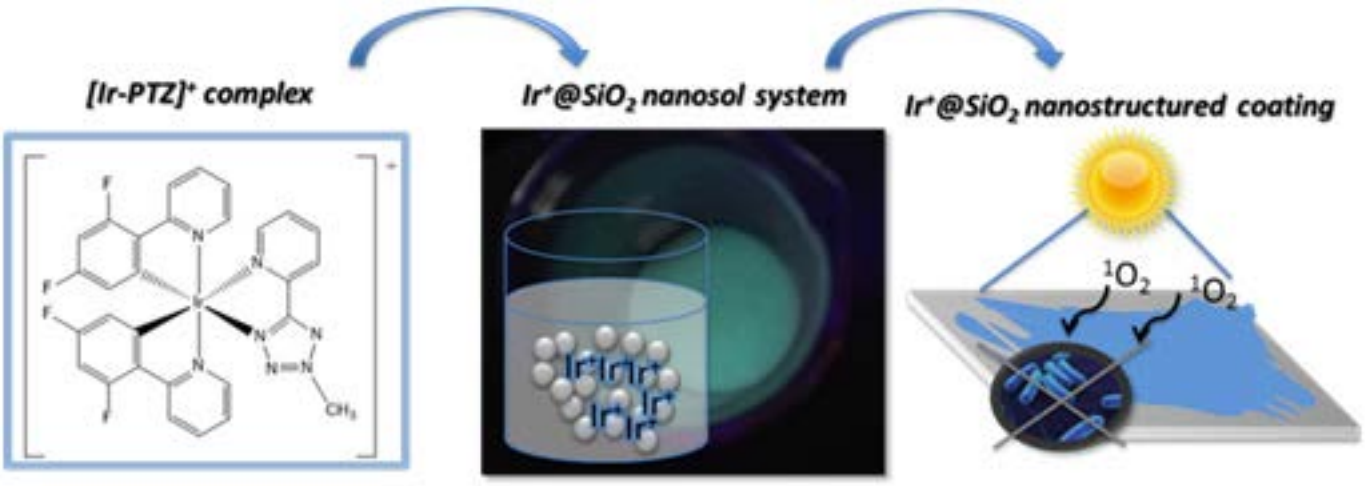

Figure 1: Scheme of all steps inside the transfer of Iridium(III) complexes into Ir@SiO2NPs systems (first as liquid state and then as textiles coating).

Key words: Iridium(III) complex, Silica, Luminescent textiles, Antibacterial Activity, Franz cell, Nanotoxicology, Skin

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Synthesis of Early Transition Metal Diboride Nanocrystals

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Group IV and V metal diboride (MB_2) have very high melting point (>3000 °C), high hardness, good chemical stability, thermal and electrical conductivity. CMCs based on these phases are expected to be potential candidate materials for applications at extreme temperature and harsh environments in the aerospace industry [1]. Availability of submicrometric/nanometric boride particles has indeed the potential to improve several stages of ceramic processing, [2] or for instance to facilitate the sintering of those ceramics, [3] due to enhanced particle reactivity. The synthesis of MB2 nanocrystals (M=Zr, Ti, Hf, Nb, Ta) using $NaBH_4$ and the respective metal oxides at atmospheric pressure was studied at temperatures between 400 and 1000 °C. [7] Reaction products were analyzed by x-ray diffraction, the crystallite size was determined after Rietveld refinement of diffraction patterns, whilst the morphology was analyzed by scanning and transmission electron microscopy. The reaction occurs first via decomposition of NaBH4, followed by the formation crystalline ternary species Na_2MO_3 (M=Ti, Zr, Hf), $NaMO_3$ (M= Nb, Ta) and several sodium borates at the early stage of the synthesis at 500-600 °C. Metal diboride (MB_2) and sodium meta-borate ($NaBO_2$) are the final products at 700 °C.

Parole Chiave: UHTC, nanostructured materials; solid state reactions; Rietveld refinement; BET;

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Safe-by-Design Approach for Winning the Nanorisk Challenge

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The unique properties of nanomaterials (NMs) arise from their nanoscale. Unfortunately, such peculiarity is also the main source of their potential toxicity when they come in contact with biological systems. Safe-by-Design (SbyD) strategies are very promising solutions for the preventive risk management of nanoparticles and nano-related products [1]. They aim to design NMs with the desired functional properties, but with reduced (or no) toxicity and/or potential exposure. In order to reach such an ambitious goal a lot of aspects have to be taken into account and multidisciplinary efforts have to be put in place. We made the first steps in this direction in the frame of two European collaborative research projects addressed to mitigate the risk from NMs for the human health in workplaces (SANOWORK) and to make the production of NMs sustainable (SUN). Nevertheless a right compromise between the potential reduction of risk and preservation of expected functional properties should be achieved. At this aim, in this work, we suggest a step-wise approach as supporting tool for the individuation and selection of a SbyD strategy in relation with the physicochemical properties of NMs, their evolution in testing media, and their biological reactivity, as well as their technological functionality. Moreover, we will present some results taken by case studies developed in the EU projects abovementioned where we modified commercial NMs with inorganic or organic coatings to control their biological reactivity or tried to limit exposure by purifying nanosols from the excess of toxic ions or controlling powder dustiness by granulating pristine nanopowders. In particular, we coated titanium dioxide (TiO_2) with silica (SiO_2) and copper oxide (CuO) with several organic capping agents (sodium citrate, sodium ascorbate, PVP, PEI) and ultrafiltered silver (Ag) nanosol to remove silver ions in excess. We measured and compared the physicochemical properties of pristine and modified samples and their evolution in testing media (water, biological and environmental fluids) in terms of size, zeta potential, and risk-relevant physicochemical properties, such as ion distribution and reactive oxygen species (ROS) production, in order to evaluate the effects of the treatments applied.

Parole chiave: Safe-by-Design, Nanomaterials, Nanorisk.

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Industrial Materials: the Challanges for *SMART* Coatings

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Today, many different industries need of innovative and flexible solutions making of the same bulk material a new *multifunctional* one, with improved added value, to be easily integrated in the production lines. Wettability is a fundamental property of a solid surface, whose control plays a key role in sectors such as the ceramic and glass ones, aerospace, naval or maritime, electronic and mechanical, and so on. The assessment of the scientific criteria to modulate the wetting - which depends in a complex way, other than on the contact fluids, on the surface chemistry and its structural features interacting with the surrounding environment - is among the biggest challenges of innovation in the field of materials' science.
In the last ten years, the *Smart Surface* group at ISTEC CNR focused his activity on processing and technical solutions mimicking the outstanding ability of living organisms to repel water and/or oily substances, trying to replicate it on synthetic materials. To design low-wettable materials ISTEC CNR researchers drew inspiration from the perfectly, mostly hierarchically organized structures (*Lotus* leaf, *Nephentes* plant, *Shark* skin) allowing the natural organisms to actively interact with the surrounding environment. Current knowledge highlights that high static contact angle (CA>150°), CA hysteresis (difference between the advancing and receding CAs in dynamic sliding/rolling of a fluid drop) lower than 5° and an extremely reduced surface energy are the basic parameters to produce i.e. self-cleaning, de-icing, anti-fouling o anti-soiling materials, low friction components, materials with attitude to drag or noise reduction, etc, these properties generating great potential in strategic industrial sectors.
The know-how developed at ISTEC CNR [1-5] together with the current activities, at national and international level, relating with the design of *amphiphobic* glasses and ceramics, metals and alloys - simoultaneously behaving as extremely repellent to water (superhydrophobicity) and low-surface tension liquids (oleophobicity) - are summarized in this talk. Nano-oxides suspensions with an average particle size of less than 30 nm, eventually coupled with perfluorinated, lubricant compounds, have been used to modify the material surfaces giving rise to *solid-liquid-air* working interfaces or, alternatively, to *solid-liquid-liquid* ones. Dip coating, automated spraying, roller printing for flexible substrates are available as deposition techniques at ISTEC CNR. It is worth to underline that prototypes up to 50 x 40 cm^2 can be realized in our labs. Optically transparent, homogeneous, nanostructured organic/inorganic hybrid coatings, with a thickness commonly in the 200-300 nm range that, if any, can be implemented up to some microns, are generated by sol-gel method [2, 3], followed by thermal processing and introduction of low energy elements. Static contact angles with water as high as 178° and 140-150° with oil are commonly reached, coupled with excellent de-wetting, certified by the contact angle hysteresis lower than 5°. A full characterization of the surface chemistry is undertaken by XPS analyses, highlighting the different components of the hybrid coating and their functional role, while FESEM observations estimate the coating's thickness (300-400 nm) and their structural features (*flower-like* lamellas, agglomeration of spherical nanoparticles, shark-skin features, etc). The potential applications of *amphiphobic* materials clamp on durability under different conditions (i.e. chemically aggressive environments, presence of mechanical stresses, friction effects, etc), so that the research team is even more committed to design robust products able to keep unchanged their performances over the time. Thus, the approach to *smart* materials as

structural parts or components, the assessment of their performances in conditions close to the real ones, the understanding of their full potential, etc, require multidisciplinary competences, availability of equipments and facilities belonging to industrial sectors even far from those already assessed. These circumstances suggest that appropriate networking actions, at different level from the research to the industrial one, will be necessary in the next future in order to bring great convenience in many strategic industrial processes and enhance the impact of *smart* surfaces innovation.

Parole chiave: Smart surfaces, Amfifobicity, Superhydrophobicity, Oleophobicity, Hybrid coatings

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Geopolymer Composite Oxygen Carriers for Chemical Looping Processes

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Chemical Looping Combustion (CLC) allows the inherent separation of CO_2, through the heterogeneous oxidation and reduction of an oxygen carrier (OC) which transfers oxygen for the combustion from air to the fuel [1]. In this work, geopolymer (GP) composites were proposed as a novel class of OCs for CLC. GPs are quasi-amorphous and nanostructured ceramic materials obtained by alkaline activation of alumino-silicate precursors through an easy, low-cost and green process at low to moderate temperature (25-100°C). They possess optimal features for this application as a diffused meso-porosity and an high surface area, combined to substantially high mechanical strength, abrasion resistance and stability to temperature up to 1000°C [2]. Within the composite the GP phase served as support matrix, while Fe_2O_3 and Mn_2O_3 were selected as non-toxic and largely available active phases. A relevant advantage of GPs lies in their production process. In fact, while OCs are generally produced through conventional methods based on the impregnation of supports with metal salts, the GP composites were produced through a one-step synthesis, thereby drastically optimizing the time and the cost of the overall process. Together with the distinct Fe and Mn-based composites, the two oxides where combined in a mixed OC in order to evaluate the synergy between them. Laboratory tests of the novel OCs were carried out in a CLC plant for the combustion of a CO rich syngas at 800, 850 and 900°C. The materials showed a suitable stability to the reaction conditions, with no cracking or agglomeration after repeated CLC cycles. The tests pointed out the better performance of the Mn-based oxygen carrier at 900°C, which achieved efficiency in CO conversion up to 98%, and exhibited the ability to release O_2 in inert conditions. Moreover, the GP matrix resulted to actively influence the OC behavior through the formation of Mn-Si phases, which could improve the oxygen release capacity of the material. The Mn-Fe sample reached performance very close to the Mn-based one, probably related to the formation of an intermediate Mn-ferrite phase. The release of O_2 under certain conditions of temperature and pressure opens the possibility of utilization in processes different from CLC (e.g. O_2 separation from air).

Parole chiave: CLC, Geopolymers, Iron oxide, Manganese oxide

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Highly Efficient Emissive Solid-State Organic Materials: New Achievements @ ISTM

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High tech applications of light emitting materials very often require their use in the condensed phase. However, frequently, luminogenic molecules are highly emissive in dilute solutions or in nanostructured host-guest systems but they become weakly or even non-emissive in the solid aggregated. However, recently, an unusual behaviour opposite to the ACQ has been observed for a still limited number of luminogens which have been found to emit more efficiently in the solid state than in solution according to aggregation-induced-emission (AIE). Particularly relevant in this field are aggregation-induced room temperature phosphorescent (RTP) organic materials due to their potential value in organic light-emitting diodes (OLEDs), optical storage, bioimaging, sensors, security, and many other applications. They are also very good candidates for replacing phosphorescent organometallic complexes containing expensive and generally toxic metals. However, the properties of organic solids in the triplet excited state are affected by many factors and, therefore, it remains a great challenge to design/prepare highly efficient organic RTP solids.
In this context, we have isolated a simple pure organic molecule, namely cyclic triimidazole ($C_9H_6N_6$), which is weakly emissive in solution but highly so in crystals (QY equal to 30%). The nature of the emission has been verified by time resolved emission spectroscopy revealing the presence of both fluorescence and phosphorescence, this latter showing an impressive ultralong lifetime (up to 1 s at r.t. in air). By combined experimental, structural and theoretical calculations, the crystallization induced ultralong RTP of the compound has been attributed to its H-aggregation [1]. We will present the results obtained on a series of derivatives of this prototype for the purpose of consolidating and extending the scope of cyclic triimidazole as a promising scaffold to be used for devices implementation.
On the side of organic fluorescent organic materials, we have recently developed an extended family of novel compounds [2] which, similar to the archetypal AIE tetraphenylethene, are formed of a central olefin stator and decorated with either three or four rotors. These rotors, being either electron-rich substituted benzenes, or electron-withdrawing functional groups (esters, ketones, cyano groups) confer a “push–pull” character to the molecular structure. Their molecular optical properties and solid state emissive behavior will be presented.

Parole chiave: aggregation-induced-emission • room temperature phosphorescence • H aggregates • halogen bonding • cyclic triimidazole • dual fluorescence

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Membrane Systems and Mesenchymal Stem Cells in Tissue Engineering

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Advanced biohybrid constructs made of polymeric membranes and human mesenchymal stem cells, in both homotypic and heterotypic co-culture systems with primary cells, will be presented in this work as an ambitious attempt for the creation of self-renewing human tissue models.
MSCs represent an easily accessible and potentially autologous adult cell source, very attractive for their ability to activate and differentiate into multiple tissue cell types, and very engaging for their influence in improving the morpho-functional behaviour of in vitro cell constructs by means of the secretion of fundamental growth factors and signalling molecules.
Polymeric micro and nanostructured membranes provide the mechanical support and the biochemical stimuli able to modulate cellular responses affecting cell adhesion, proliferation and differentiation. Suitable topographical, physico-chemical and mechanical membrane properties are critical for directing stem cell fate by transmitting specific signals. Furthermore, engineered membrane bioreactors compartmentalize cells favouring the physical separation of MSCs from the primary cells by means of porous semipermeable membranes that ensures in the meantime the selective mass transfer of the secreted paracrine factors, and thus mimicking the in vivo physiological stem cell niches. Moreover, novel membranes with double porous morphology entrap MSCs like in artificial niches.
Engineered microenvironments made by the combination of porous membranes with stem cells were realized for the creation of skin and liver in vitro models. Bioengineered skin substitutes were realized by combining biodegradable membranes and MSCs isolated from human dermis, the human Skin derived Stem Cells, in homotipic and co-culture systems with keratinocytes, for the creation of dermal and dermal/epidermal constructs. Organotypic membrane bioreactors utilizing primary human hepatocytes in direct and connected co-culture systems with human endothelial and MSCs offered interesting opportunities for the design of bioartificial livers as in vitro models with high morpho-functional performance.

Keywords: Membrane, Bioreactor, Mesenchymal Stem Cells, Co-culture, Skin, Liver

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AMECRYS – Project Overview and Main Activities Performed in the First Year

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AMECRYS is a project coordinated by CNR, funded by the European Commission's Horizon 2020 Programme in the framework of Future and Emerging Technologies actions (FET-OPEN), which supports the early-stages of the science and technology research and innovation around new ideas toward radically new future technologies.
The primary goal of the AMECRYS' Consortium is to contribute in revolutionizing currently used downstream practices in biopharmaceutical productions, mainly based on expensive and cumbersome multi-step batch chromatography platforms, by developing an innovative Continuous Template-Assisted Membrane Crystallization process as key-unit.
The research activity is focused on the downstream processing of monoclonal antibodies (mAbs), one of the most important classes of therapeutic proteins in modern medicine, which are used in a wide range of diseases including cancer, cardiovascular, autoimmune, and inflammation. The fundamental idea of the AMECRYS approach is based on the combination of two innovative concepts: (1) membrane-assisted crystallization, a radically new separation technology based on the use of macroporous hydrophobic membranes which allows the accurate control of supersaturation by solvent removal in vapour phase, and (2) template-assisted crystallization by engineered mesoporous silica 3D-nanotemplates, to enable the crystallization of structurally complex therapeutic proteins from multicomponent solutions.
The AMECRYS network involves two public research organizations, four academic institutions, and three industrial/SME from four European Countries (Italy, England, Belgium, and France).
In this presentation, an overview of the main research activities and achievements obtained during the first year of project's implementation by the CNR unit will be discussed.

Parole chiave: Bioseparations, Membrane preparation, Monoclonal Antibodies purification

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A Novel Method to Characterize the Gas Transport in Advanced Membrane Materials

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The increasing importance of membrane-based gas separation processes necessitates the development of novel materials with enhanced performance, in terms of higher permeability and higher selectivity. In the last several years, our attention has been focused on a completely novel class of polymers, defined as Polymers of Intrinsic Microporosity (PIM), with high free volume, as a result of a combination of an extremely rigid and highly contorted polymer backbone. In collaboration with the pioneers in this field, the effect of various structural variations of the polymers on the membrane performance has been studied, incorporating different contortion sites,[1,2] changing the backbone structures[3] or adding bulky spacers to keep the backbones further apart.[4] The properties of these materials have been further enhanced by the chemical modification of the functional groups[5,6] or by the inclusion of porous nano-fillers to yield mixed matrix membranes.[7]
A fundamental requirement for the development and the application of novel membrane materials is a good understanding of their structural and performance properties. In this light, the present paper will discuss a novel gas permeation instrument, based on mass spectrometric analysis of the permeate gas composition. This instrument has the unique capacity to determine the diffusion coefficients of the individual gases from a mixture in the membrane material. Therefore, it is able to identify the origin of anomalous gas permeation observed in some of the novel polymer membranes, either in terms of diffusion or in terms of sorption. The results of the novel measurement technique will be viewed in the light of more general structure-property relationships of the materials and will be supported by molecular modelling studies.[8]

Parole chiave: Membranes, polymers of intrinsic microporosity, gas separation, diffusion

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Alternanza Scuola Lavoro: si Riducono le Distanze tra Ricerca e Scuola

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L' Alternanza Scuola Lavoro è diventata obbligatoria con l'approvazione della legge n. 107/2017 nota come "La Buona Scuola". Gli Istituti di Ricerca Pubblici possono essere dei partner educativi della scuola nella realizzazione di progetti/percorsi di ASL. L'offerta di moduli formativi per ASL da parte degli Istituti di Ricerca si motiva con l'obiettivo di accrescere l'interesse dei giovani allo studio delle discipline scientifiche, mentre acquisiscono nuove competenze lavorative. D'altra parte queste attività formative/lavorative possono essere viste come attività di divulgazione delle nuove scoperte scientifiche verso la cittadinanza da parte degli Istituti di Ricerca. Nella presentazione saranno relazionati i progetti/percorsi educativi svolti nell'anno scolastico 2016-2017, presso L'Istituto di Cristallografia (sede di Monterotondo), dagli studenti degli Istituti Scolastici delle provincie di Roma e Rieti. A dimostrazione delle nuove competenze acquisite dagli studenti, che hanno frequentato questi percorsi, saranno mostrati alcuni dei prodotti didattici da loro realizzati. Tra questi prodotti didattici la mostra multimediale "Il Lato Rosa della Scienza" presentata alla Notte della Scienza 2017 presso l'Area della Ricerca di Roma 2 (Tor Vergata). Gli studenti delle classi III e IV del Liceo Scientifico G.Peano durante il periodo di ASL presso IC hanno realizzato la mostra con gli strumenti di scrittura collaborativa accademica.
Per lo svolgimento dei percorsi formativi si sono utilizzate le nuove tecnologie di internet, note con il nome web 2.0, sulla piattaforma informatica per la formazione dell'Istituto di Cristallografia. Il software utilizzato è quello adottato da molte università, Moodle, ma la configurazione hardware dei server è stata realizzata e modificata dal gruppo Smart ELab dell'IC per ottenere alte prestazioni e alta affidabilità.

Parole chiave: Alternanza Scuola Lavoro, Formazione.

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Uno dei compiti istituzionali degli enti pubblici di ricerca, è la promozione della diffusione della conoscenza attraverso proprie iniziative editoriali. Nella classificazione di prodotti editoriali accademici sono presenti, oltre agli articoli su riviste scientifiche, le presentazioni e i poster presentati a convegni, monografie, libri ecc. Il progresso tecnologico nell'ambito della comunicazione e la diffusione della rete internet rende disponibile alla comunità scientifica la produzione e la diffusione in proprio dei prodotti editoriali accademici. L'auto-pubblicazione dei contenuti scientifici è ora possibile attraverso l'uso di piattaforme informatiche per la gestione di tutto il processo editoriale di produzione e distribuzione di riviste e monografie digitali. Attualmente sono disponibili anche piattaforme informatiche specializzate per la scrittura collaborativa scientifica. Con queste ultime è possibile realizzare prodotti editoriali scientifici di alta qualità tipografica in modalità collaborativa. Con piattaforme per la scrittura collaborativa si devono intendere software che consentono a più autori di scrivere contemporaneamente sullo stesso documento, anche in parti diverse dello stesso, mantenendo traccia delle modifiche. Il gruppo di lavoro Smart eLab dell'Istituto di Cristallografia ha sperimentato con successo due piattaforme informatiche per la gestione delle riviste scientifiche e per la scrittura collaborativa accademica. I risultati della sperimentazione e i vantaggi dell'uso di queste tecnologie digitali per gli istituti di ricerca saranno esposti in questo lavoro.

Parole chiave: Comunicazione Scientifica, Editoria Digitale, Scrittura collaborativa Accademica

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Computational Methodologies for the Characterization of Polycrystalline Materials in Software Developed by the Institute of Crystallography

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Innovative methodologies have been developed and implemented in computer programs aiming at providing efficient computational tools for a wide range of applications in the field of the characterization of polycrystalline materials. The software, based on sound theoretical principles, developed according to the most recent and advanced programming languages and supported by a high level of automatism which makes its use simple also to non-expert in crystallographic knowledge, is worldwide used. Moreover, it is continuously improved in terms of computational and graphic performances and tested on our powder diffraction data bank. **EXPO**[1] is a software devoted to reveal the atomic structure of compounds available in the form of microcrystalline powder, by starting from only the chemical formula and the experimental diffraction profile. It is able to investigate small molecules (up to 100 non-H atoms in the asymmetric unit), inorganic as well as organic and metalorganic. It can execute the following steps: 1) identifying the crystal cell parameters; 2) determining the space group; 3) solving the structure by locating the atom positions; 4) refining the crystal model. Very recently its use has been crucial for deep understanding of new rare-earth tricalcium phosphates $Ca_9RE(PO_4)_7$ (RE = La, Pr, Nd, Eu, Gd, Dy, Tm, Yb)[2]. **QUALX2.0**[3] is a software aimed at identifying the crystal phase(s) present in a powder sample. It automatically locates peaks in the experimental diffraction profile, subtracts the background noise, makes a search in crystal phase databanks and brings out the chemical phase(s) which best match the peaks in the experimental pattern. Its use is of utility for chemistry, pharmaceutics, mineralogy, forensic science, cultural heritage. An online version of *QUALX2.0* is also in progress. One of its recent applications has regarded novel mixture of silicates, labelled Li_6MnSi_5, to be proposed as alternative cathodes for Li-ion battery[4]. We are now developing the new online software Open Chemistry Database, **OChemDb** dedicated to collect, to make available by statistical tools and to manage crystal-chemical information coming from the CIF files contained in the Crystallography Open Database (COD, http://www.crystallography.net/cod/). OChemDb can be used for searching and analyzing crystal-chemical information (bond distance, bond angle, space group, ..) of structures already solved, to be used for different scientific purposes.

Parole chiave: crystallographic software, crystal structure solution, qualitative analysis, crystal chemical database

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Molecular Modeling and Bioinformatics Research Group ICB Sassari

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The molecular modeling group present at the ICB of Sassari has been formed since 2000 by Roberto Dallocchio and Alessandro Dessì. Due to their specific expertise in docking, virtual screening and molecular dynamics they support various research groups working at the Institute of Biomolecular Chemistry, and different, national and international, research groups. In collaboration with medicinal chemistry groups, they currently work on the design of novel biologically active compounds as drugs prototype on HIV-1 Integrase field, Carbonic Anhydrase, Influenza Virus PA Endonuclease, and Malaria. They also collaborate with agrochemistry groups for studies of fungal pathogens and with chemistry groups for the mechanistic aspect of halogen bond-driven interaction. For these groups, they performed several computational studies (conformational analyses, docking procedure, and molecular dynamics) and drug discovery methods (Structure-based Drug design). This applied computational approach is used in all steps of the drug research: particularly (structure-based drug design), on the drug optimization and for a better interpretation of biological results. The research goal focused mainly on the calculation of models, by computer facilities (serial and parallel computing resource present in Area) using software such as Gaussian, Amber, Autodock etc. As a group, they were also involved in the production of code as tools for data analysis of calculated data and pharmacological activities and in the generation of graphical interfaces to simplify the use of different processing.
Topic: Computational Modeling

Keywords: Structure-based drug design, docking, virtual screening, molecular dynamics

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Computational Study of Syk Inhibitors in Combination Therapy, their Interactions for the Design of Potential anti-Malaria Drugs

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In silico studies were based on different approaches to molecular modelling, to analyze and to optimize the interaction ligand-protein and obtain the highest efficacy in vitro. The preliminary study confirmed the validity of the model used. The Syk-ligand interactions highlighted in this study could provide an additional tool to discover new molecules as potential Syk inhibitors, and would guide the synthesis of novel Syk-targeted compounds by shortening the research time and by reducing cost. Together with other traditional strategies, computational approaches demonstrated their utility in the modern drug discovery of novel and potent inhibitors. In particular, virtual screening (VS) is one of the most interesting computational tools for rapid discovery of novel and original chemical entities provided of potential activity. This method is used to find ligand in compound libraries, commercial and not, natural or not, in order to increase the hit rate in biological assays. On these bases, the virtual screening might be performed by using AutoDock4 for virtual screening or VINA software. The most promising hits identified during the docking or the virtual screening will undergo an extensive refinement by molecular dynamics techniques. This approach, particularly, is focused on evaluating binding free-energies, to be compared with those obtained during the analysis of docking and VS, in order to validate the approach and to suggest possible improvements to the scoring functions of the docking procedure.

Keywords: Docking, Virtual Screening, Modelling, Syk, malaria, descriptors

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Recent Modeling Progresses in the Areas of Advanced Materials, Chemistry and Energy, and Green Chemistry

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We briefly illustrate three recent modeling developments and works of interest for three main areas of DSCTM.

The first concerns the extension[1] of the Source Function (SF) tool[2] to the analysis of the electron spin density (ESD). Within this approach, the ESD value at a point in a system may be seen as determined by a local Source Function for such density, operating at all other points of space.[1] Integration of the local Source over Bader's quantum atoms measures their contribution in determining the spin density features at any system's location. This novel tool, along with a further decomposition of the atomic sources in *magnetic* and *relaxation/reaction* components provides interesting insights on the electron spin delocalization from paramagnetic to non-magnetic centers and on ESD polarization mechanisms.[3] It also highlights their strong dependence from the ESD quality.[3] Application to the analysis of the *theoretical* spin density in two azido Cu(II) dinuclear complexes has been recently presented, in comparison to the ESD obtained from Polarized Neutron Diffraction experiments.[3] Deciphering the mechanisms through which spin information propagates through a descriptor based on an observable, rather than on an orbital model approach, is of paramount importance in *advanced materials* research.

A second contribution concerns the modelling-driven search of optimal metal-free electrodes for Li-ion batteries. Organic electrode materials have started to gain considerable attention in the last few decades as they can originate from environmentally friendly and abundant resources (biomass) and may efficiently improve the cycle life of batteries (with much reduced cost and greenhouse gas emission). Our integrated approach consists of DFT computations combined with a continuum SMD solvent model to evaluate the redox properties of a series of organic derivatives followed by an analysis of their electron and electron spin densities. On top of this, a Bader's energy decomposition analysis of the initial and reduced forms energies is performed to unearth key parameters governing voltage ranges and tunability. Within this approach, we have *a)* tuned the optimal positions for carbonyl group insertion and C/N replacement into rings of pentalenediones;[4] *b)* identified potentially low-/high-redox potential electrodes in some quinoneazine derivatives by modulating the nature of the bridge between carbon atom rings[5] and *c)* rationalised the relationship between redox potential and isomerism/(antiaromatic/aromatic) effects in different naphtho-/biphenyl-/biphenylene systems.[6] The whole methodology is of clear interest for the areas *Chemistry and Energy* and *Green Chemistry*.

The third contribution concerns the discovery of the first neutral thermodinamically stable (for P >113 GPa) compound of helium, Na_2He, and the rationalization of its geometrical and electronic structure, in terms of a chemical bonding analysis.[7] Na_2He structure has been predicted theoretically through a systematic search for stable He compounds using a variable-composition evolutionary structure prediction algorithm. Prediction has then been experimentally confirmed by loading Na into a He medium and compressing the mixture up to 155 GPa in a laser-heated Diamond Anvil Cell (DAC), using Synchrotron XRD and Raman

spectroscopy to monitor sample evolution.[7] Na_2He structure resembles a 3D checkerboard with Na_8 cubes alternatively filled with He or allocating an interstitially localized electron pair, indicated by the presence of a non-nuclear charge density maximum, Electron Localization Dunction (ELF) values close to 1.0 and a massive charge density accumulation in the deformation density map. Upon Na_2He formation, fundamental structural and charge density rearrangements take place. Indeed, the Na_2He structure is not related in any way to that of high-pressure sodium, and a product *vs* reactants comparison of QTAIM atomic volume and charges reveal important changes (up to 0.15 |e| and 0.5 $Å^3$). These evidences, along with the high exothermicity of the reaction (0.4 eV at 300 GPa) hint for Na_2He not being classifiable as an inclusion compound, but as a true chemical compound. Presence of He atoms causes strong electron localization and makes this material insulating. It may be envisaged as an electride, with localized electron pairs forming 8c-2e bonds within empty Na_8 cubes.[7] Studies of novel compounds under high pressure and interpretation of their exotic chemical bonding features is of great relevance in *advanced materials research*.

Keywords: modeling, chemical descriptors, spin density, source function, spin delocalization and polarization, Li batteries, metal-free organic electrodes, Helium compounds, High pressure, electrides

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First Principles Modeling of Organohalide Lead Perovskites for Photovoltaics Applications

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Hybrid AMX_3 perovskites (A=Cs, CH_3NH_3; M=Sn, Pb; X=halide) have in the last two years revolutionized the scenario of emerging photovoltaic technologies, demonstrating certified 17.8% efficient solar cells, with very recent claims of 24% efficiency. These efficiency values are effectively competing with existing thin film technologies, such as CIGS or CdTe, and definitely outperforming a-Si solar cells. The $CH_3NH_3PbI_3$/ $MAPbI_{3-x}Cl_x$ perovskites have dominated the field, while the similar $CH_3NH_3SnI_3$ has been less explored for photovoltaic applications. Replacement of Pb by Sn would facilitate the large uptake of perovskite-based photovoltaics. Despite the extremely fast progress, the materials electronic properties which are key to the photovoltaic performance are relatively little understood. Density Functional Theory electronic structure methods have so far delivered an unbalanced description of Pb- and Sn-based perovskites. We developed an effective GW method incorporating spin-orbit coupling which allows us to accurately model the electronic, optical and transport properties of halide perovskites, opening the way to new materials design.[1] In particular the different $CH_3NH_3SnI_3$ and $CH_3NH_3PbI_3$ electronic properties are discussed in light of their exploitation for solar cells, and found to be dominantly due to relativistic effects.
By applying our computational approach we moved to investigate the effect of the chlorine doping for the mixed halide perovskites ($MAPbI_{3-x}Cl_{x3}$),[2] the role of the different A cation (A= $CH_3NH_3^+$, $HC(NH_2)_2^+$, Cs^+), and the nature of the perovskites/TiO_2 interface.[3] The overall picture of our theoretical investigations underlines a crucial role of computational investigation, offering the possibility of performing predictive modeling simulations, in which the properties of a given system are simulated even before the materials laboratory synthesis and characterization. At the same time, computer simulations are shown to offer the required atomistic insight into hitherto inaccessible experimental observables.

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Charge-displacement Analysis: a simple Tool to Reveal Charge Transfer Effects throughout the Whole Periodic Table (from Helium to Oganesson).

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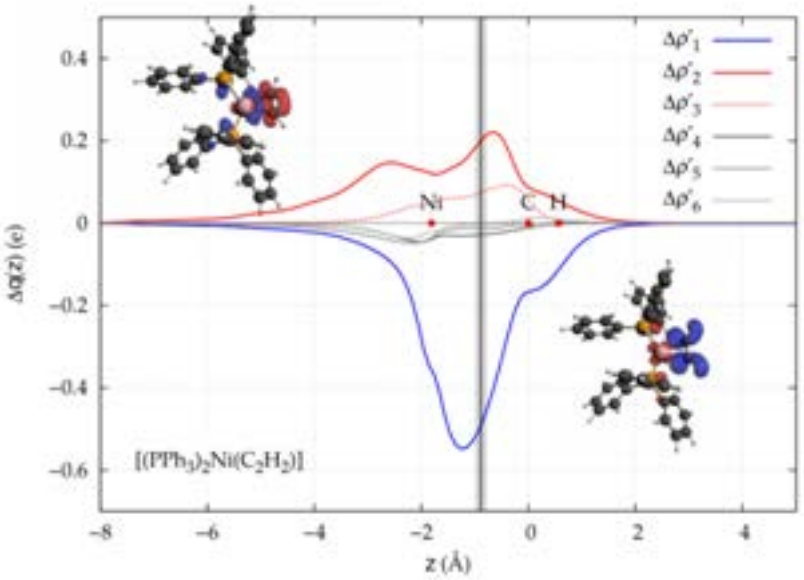
Charge-displacement (CD) analysis was introduced almost ten years ago in order to characterize the chemical bond between noble-gas (Xe) and a noble metal (Au) in Xe-AuF [1]. It is a simple yet powerful tool to reveal and quantify the charge transfer component of the interaction in chemical regimes, from gas phase water's van der Waals complexes, electronic excited states to the super-heavy elements chemical characterization. The method is based on a partial progressive integration of the electron density changes that accompanies intermolecular interactions. Recently, charge-displacement analysis has been employed to analyze on quantitative grounds the Dewar-Chatt-Duncanson components of transition metal coordination complexes [2]. The CD method provides clear-cut measures of donation and back-donation charges that show a stringent correlation with selected experimental observables [3, 4]. The method has been extended to the relativistic four-component Dirac formulation and some preliminary results of this new implementation will be presented.



Parole chiave: Legame Chimico, catalisi, effetti relativistici.

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L'impegno dell'Istituto di Cristallografia nei Beni Culturali

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La conservazione del Patrimonio Culturale è un compito di fondamentale importanza per le società moderne. Tale patrimonio inteso come Beni Culturali (B.C.), riflette la cultura, la storia passata e presente e rappresenta la principale eredità da tramandare alle generazioni future.
L'approccio a tale attività è indubbiamente multidisciplinare e in questi ultimi anni l'Istituto di Cristallografia (I.C.) sezione dell'Area di Ricerca CNR di Montelibretti, collaborando con le Soprintendenze di Roma, e dell'Etruria meridionale, si sta impegnando su diversi fronti.
Un aspetto molto importante riguarda l'applicazione di metodologie analitiche nelle spettroscopie a raggi X (XRF e XRD), l'imaging a raggi X (radiografia), la riflettometria IR e UV che è affiancata allo sviluppo di nuova strumentazione per lo studio di materiali dei B.C. (con particolare riferimento a pigmenti, metalli, ceramiche e materiali lapidei), al fine di determinarne lo stato di conservazione, le cause ed i meccanismi del loro deterioramento. Questo ha portato alla costituzione dell'ICLA (I.C. Laboratorio di Archeometria). La strumentazione a disposizione del laboratorio e la sua attività sono illustrate al sito http://www.icla.ic.cnr.it/.
La collaborazione con le Soprintendenze, formalizzata con apposite convenzioni, ha permesso di lavorare a stretto contatto con archeologi e restauratori sia presso l'ICLA, sia *in situ*. Dal 2015, durante la campagna di scavo, l'I.C. ha allestito una sezione dell'ICLA nel casale di proprietà demaniale che si trova nell'area archeologica di Crustumerium (via della Marcigliana 1052 – Roma) per l'analisi di reperti appena estratti dal suolo al fine di progettarne il miglior intervento di recupero e conservazione.
Un altro aspetto è l'attività di disseminazione e valorizzazione della ricerca, rivolta sia a settori specifici, sia al vasto pubblico. In particolare il gruppo ICT (Information and Comunication Tecnology) dell'I.C., sfruttando le proprie competenze sulle trasmissioni radio via Wireless e con la collaborazione di uno sponsor, la *Skylinewebcams*, ha realizzato la ripresa video online degli scavi archeologici di Crustumerium (campagna di scavo 2016 e 2017) e di quelli di Pyrgi (Castello di Santa Severa RM) nel 2017. Questa attività ha la duplice funzione di controllo remoto dello scavo e di valorizzazione del sito. L'attività degli archeologi sugli scavi di Crustumerium nel luglio 2016, visibile in tempo reale in tutto il mondo, ha permesso di collegare i visitatori della mostra "CRUSTUMERIUM, Death and Afterlife at the Gates of Rome" presso la Ny Carlsberg Glyptotek di Copenaghen con gli archeologi per domande e informazioni sul lavoro in campo.

Parole chiave: X-rays, XRF, XRD, archaeological excavation monitoring

Ringraziamenti:
Soprintendenza Archeologia, Belle Arti e Paesaggio per l'area metropolitana di Roma, la provincia di Viterbo e l'Etruria Meridionale, Soprintendenza Speciale per il Colosseo e l'Area Archeologica Centrale, gruppo ICT dell'IC

Cultural Heritage and Territory: Environmental Analysis and Dating in the Qanats of the Kavir Desert Oasis (Iran)

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The Qanats are antique hydraulic systems. Farmers use them to carry water from the ground floor to the cultivated land, using the force of gravity. Many of them were built over 2,500 years ago in Iran and then spread throughout the Middle East, in Central Asia, North Africa and isolated cases in Sicily, Andalusia and Mexico.
The Qanats are impressive hydraulic engineering works that played a significant social and economic role in the arid regions, but they are currently in crisis for two main reasons: the large demographic growth of the countries concerned and the climatic effects due the overheating of the Planet.
During the missions in Iran, we carried out the following investigations:

- Evaluation of chemical and physical parameters of the water;
- Presence of Radon gas in water and tunnels;
- Analysis of build materials;
- Exploration and survey of significant hypogeal tracts;
- Topography of structural features and surface;
- Measurement of the water flow and hydrogeological characterization of the area;
- Date of archaeological findings with the thermo-luminescence technique;

During the missions in Iranian territory we placed several devices, both indoor and outdoor, to detect a lot of valuable data. The instruments were placed in three locations in the north: the city of Shahrood, the city of Bear Jomand on the edge of the desert and the oasis of Torud in the desert of Kavir.
Another study we are carrying out in the Yazd region of central Iran, aims to monitor the variations in the flow and quality of groundwater in relation to the climate changes in the mountains where the aquifers feeding the Qanats are. The purpose of this study is to define a model for similar environmental situations, to know in advance the variations related to Qanat waters.

Parole chiave: Cultural Heritage, Environment, Iran

Riferimenti:
QANAT PROJECT: redevelopment of irrigation systems and surrounding areas, dating of artefacts and related computer cataloging (Typical Atlas of Qanats).

Ringraziamenti:
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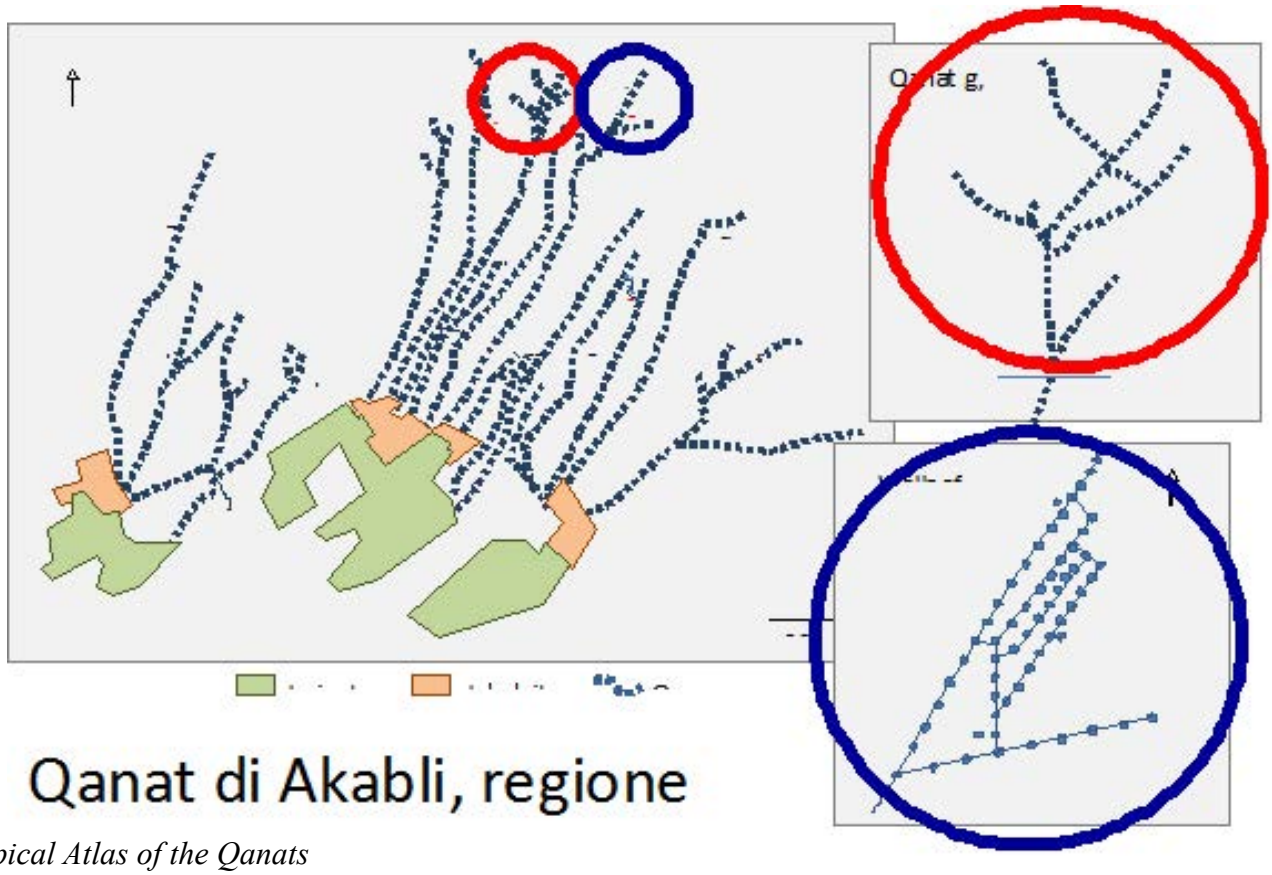
The Qanat of Dame Gam (Iran)



Typical Atlas of the Qanats

Materiali e Soluzioni Ecosostenibili per la Conservazione del Patrimonio Culturale

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Sempre più cogente è la necessità di impiegare materiali eco-compatibili, sicuri, di lunga durata e, soprattutto, alternativi rispetto a quelli attualmente in uso, spesso tossici e/o dannosi per la Conservazione del Patrimonio Culturale. In particolare, lo sviluppo di nuovi materiali e metodi per la protezione di superfici antiche (inibizione della corrosione e/o del biodeterioramento) rappresenta una risposta doverosa e necessaria alla richiesta di sicurezza non soltanto del Bene da tutelare ma anche del Restauratore e dell'Ambiente.
Il nostro gruppo di ricerca si occupa di progettazione, sintesi e validazione di nuovi prodotti e/o formulazioni ecocompatibili e a bassa tossicità per la conservazione ed il restauro. L'impiego di nanovettori per l'intrappolamento e rilascio controllato di agenti preservanti di origine commerciale sembra essere una delle strategie più promettenti per garantire efficienza nel trattamento di superfici metalliche e/o lapidee, per controllare il rilascio in funzione di modifiche nell'ambiente circostante o nella stabilità del ricoprimento di superficie e per limitare la quantità, il contatto e la dispersione di prodotti chimici nocivi. Inoltre vengono anche studiati prodotti di origine naturale (estratti da piante tipiche del Mediterraneo e/o scarti di lavorazione industriale) come rivestimenti protettivi e/o inibitori di corrosione e/o biodeterioramento di superfici metalliche e lapidee. L'efficacia di questi rivestimenti sotto forma di film sottili viene valutata mediante tecniche di analisi di superficie (XPS e SEM-EDS) e tecniche elettrochimiche (curve potenziodinamiche e spettroscopia di impedenza elettrochimica EIS). L'ambiente corrosivo è quello tipicamente marino (corrosione per attacco di cloruri) e quello derivante dall'inquinamento tipico di un'atmosfera urbana (corrosione da piogge acide).

Parole chiave: Nanoveicolazione; Inibitori di corrosione; Biodeteriogeni; Conservazione di Manufatti Metallici e Manufatti Lapidei

Riferimenti:
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Carbonatation of Ca-based Consolidants into Limestone Matrix: a SR-based Imaging Study by Micro- XRF, XANES and XRD Techniques

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In the past, consolidating products commonly used for preservation of historical limestone monuments against weathering were mostly based on synthetic organic polymers which generally lack of mechanical efficiency, physico-chemical compatibility and stability over time (1). More recently, inorganic treatments based on the in situ formation of $CaCO_3$ [starting from nano-dispersions of $Ca(OH)_2$ or solution of calcium alkoxides], have proved to be more suitable due to the higher compatibility and stability with respect to synthetic polymers (2,3). On the other side, these Ca-based consolidants have scant penetration depth and may form different $CaCO_3$ phases, including amorphous deposits and crystalline phases composed of either vaterite or calcite, or their mixtures (1-3). Amorphous $CaCO_3$ and vaterite are more soluble than calcite; moreover, differences in crystal structure between the calcitic substrate and the newly formed phases may hamper an effective cohesion of the materials. In consideration of these aspects, a careful evaluation of the physico-chemical properties of the consolidant requires highly specific and spatially resolved techniques to investigate penetration, distribution and speciation of the Ca-based compounds inside the porosity of limestone.
In this work, we proposed a multimethod SR-based approach exploiting X-ray imaging methods, i.e. μ-XRF, μ-XANES at the Ca K-edge (in scanning and full-field mode) and μ-XRD at the ESRF-ID21 beamline, to investigate at the micro-meter scale the nature and distribution of $CaCO_3$ phases inside calcitic substrates treated with two Ca-based consolidants and cured at different RH% values. Specifically we analyzed thin transversal sections of limestone specimens treated with a new consolidant formulation (based on a solution of calcium acetoacetate produced within the HEROMAT EU-project) and a commercial nano dispersion of $Ca(OH)_2$. The results from this integrated study proved to give highly valuable information for assessing at the micro-scale carbonatation of calcium-based consolidants within a calcitic matrix.

Parole chiave: limestone, Ca-based consolidants, Synchrotron Radiation, X-ray imaging methods

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